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Procedures for Comparing Combustion Emissions from Synthetic and Petroleum Fuels Phase 1

KVB, Inc., Irvine, CA

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PROCEDURES FOR COMPARING COMBUSTION EMISSIONS FROM SYNTHETIC AND PETROLEUM FUELS

PHASE I

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16. ABSTRACT The report gives results of combustion tests of petrofuels and synfuels at EPA's Research Triangle Park (NC) combustion laboratory on a 740-kW (thermal input) package boiler and a 190-kW (250 hp) stationary diesel internal combustion engine. These tests were the first in a series to develop a protocol for determining environmentally significant differences between petrofuel and synfuel combustion emission characteristics. Six petrofuels and four synfuels were evaluated. Particulate samples, obtained using a modified EPA Method 5 train and a dilution tunnel with a filter, were analyzed using Level 1 procedures with emphasis on organic constituents. Results showed that the test and sample collection procedures yielded both inconsistent sample loadings and contaminants that masked the true fuel combustion products. Corrective procedures were identified which will be used in subsequent tests.

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is responsible for helping to ensure that new substances other than food, drugs, and tobacco will not be harmful to human health or the environment. The first samples of a new group of substances, synthetic fuels (synfuels), have been produced and are expected to become commercially available within the next several years. The effects that large-scale use of synfuels will have on the environment and human health are not known (1)*. The EPA's Office of Research and Development (ORD) is conducting research on synfuels to support the Agency's evaluation and regulatory activities. Properties of liquid synfuels and of emissions from combusted synfuels are being examined, as well as the extent to which volatile, hazardous organic substances escape from the fuels during handling and storage.

Synfuels derived from coal, shale, and tar sands differ from conventional fuels in physical and chemical properties, and in the extent to which they stimulate biological activity. For example, concentrations of aromatic and nitrogen-containing compounds are generally higher in liquid synfuels than in liquid petrolem-based fuels (petrofuels) (1,2,3,4,5,6). Certain coal- and shale-derived liquids and their combustion products are more toxic, mutagenic, and carcinogenic than petrofuels, as determined by a variety of biological tests (1,7,8,9,10,11). The degree to which the fuels differ depends largely on the extent to which they have been upgraded and refined. The development of synfuels is still in its early stages, thus, the fuels that reach the marketplace may be quite different from those that are now available.

Most of the reseach on synfuels to date has been on the liquids themselves rather than on their combustion and emission characteristics. In 1981, engineers and scientists in the ORD's Industrial Environmental Research Laboratory (IERL) and the Health Effects Research Laboratory (HERL) initiated

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*Numbers in brackets are references.

a research project to investigate synfuel emissions. The primary objective of the project is to develop cost-effective procedures for comparing characteristics of emissions from synfuels and petrofuels that have been burned in conventional stationary combustors. The first phases of the project, roughly one phase per year between 1981 and 1984, focus on liquid synfuels because they have been made available in limited quantities. Synthetic gas and solid fuels will be scheduled for combustion testing as they become available.

Because synfuels will be used as supplements for petrofuels, synfuel testing during the early phases of the project will be done by comparing synfuels with conventional petrofuels. Until researchers understand more about the biological effects of the parameters they measure in emissions, judgments as to whether one type of fuel is better or worse than another cannot be made; it can only be stated that characteristics of one fuel do or do not differ from another.

When synfuels become a replacement in the market place for petrofuel, there may be public concern about the possible adverse environmental and health effects caused by burning these fuels. The EPA should be prepared to address these concerns, and this is why the project described in this report was initiated.

There will be a series of reports issued on this project. Each report will document the work conducted in a particular phase of the project. This report was compiled by KVB, Inc., based on work performed by EPA/IERL-RTP.

ABSTRACT

Combustion tests of petrofuels and synfuels were performed by EPA at their laboratory facility on a 740 kW (thermal input) package boiler and a 190 kW (250 hp) stationary diesel internal combustion engine. These tests were the first in a series of a program to develop a protocol for determining environmentally significant differences between petrofuels and synfuels combustion emission characteristics. A total of six petrofuels and four synfuels were evaluated by EPA.

Particulate samples were obtained using a modified EPA Method 5 train and a dilution tunnel with a filter. These samples were analyzed by EPA using Level 1 procedures with emphasis on organic constituents. Results showed test procedures and sample collection procedures to yield inconsistent sample loadings, and contaminants which masked the true fuel combustion products. Corrective procedures were identified which will be incorporated in subsequent test phases.

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SECTION 1.0

INTRODUCTION

1.1 OBJECTIVE

The objective of the Phase I program was to initiate the development of cost-effective procedures which would allow an accurate comparison to be made of the combustion emission characteristics of synfuels and petrofuels from stationary sources. These characteristics would include gaseous, organic and inorganic components resulting from the combustion of these two basic fuel types.

A workshop was held at the conclusion of Phase I for the purpose of reviewing the procedures and results obtained. The workshop was composed of government and industrial researchers active in synfuel utilization. Recommendations from the workshop participants were considered for incorporation into subsequent phases of the program.

1.2 APPROACH

The specific approach adopted to satisfy the Phase I program objective was influenced, to a great extent, by its comparative nature. The testing and analytical procedures would be structured to identify statistically significant differences between the emission characteristics of synfuels and their petrofuel counterparts under similar combustion operation conditions. In this respect, the ability to determine absolute levels of emission characteristics would be of less importance than the ability to detect differences.

The magnitude of the synfuel supplies available for the Phase I program required that the combustion systems be of a moderate size. In addiiton, the combustion systems employed were to be representative of the existing population of industrial steam boilers and stationary diesel engines, and were to be operated in a manner consistent with current industry practice. The moderate size of the combustion systems would also allow better control of the synfuel from a spillage and health standpoint.

This initial phase of the program was to be a preliminary effort to burn a wide range of synfuels ranging from methanol to heavy coal-derived distillates, as well as petrofuels ranging from light distillate No. 2 to heavy No. 6 fuel oils. During the combustion of these fuels, sampling procedures to obtain large particulate samples for Level 1 analysis and bioassay evaluation were to be developed. Of particular interest would be a determination of the sensitivity to detect significant differences in the combustion emissions from synfuel/petrofuels using the analytical, chemical and biological testing procedures initially proposed.

Many of the foregoing criteria could be achieved, including the analytical diagnostics, by use of in-house IERL/RTP facilities, thus, this initial phase of the program, Phase I, was performed in its entirety at IERL/RTP. A presentation of the planned Phase I work was made at the sixth EPA symposium on environmental aspects of fuel conversion technology (12).

The results of Phase I have previously been discussed at a workshop (13) where the problems encountered in the Phase I tests were discussed and recommendations made to revise the procedures for subsequent Phase II testing. Those conclusions and recommendations, as well as those of the authors of this report, will be discussed later. The proceedings of the workshop are given in Appendix A. A complete summary of all test data and a statistical analysis of the data were also prepared for the workshop and distributed to all participants. The test summary and statistical analysis are not included in Appendix A but are on file at IERL/RTP.

The combustion variables examined during the test program included combustor type and fuel type. Gaseous combustion products monitored during the program included stack oxygen (O_2), oxides of nitrogen (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THC) and sulfur dioxide (SO_2).

SECTION 2.0

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The objectives of the Phase I program were (1) to evaluate proposed procedures to obtain particulate and gas phase samples samples from an industrial package boiler and a diesel engine and (2) then analyze the samples for inorganic, organic and biological characteristics. The fuels used were a wide range of synfuels and petrofuels.

The initial work was an exploratory phase. It was not expected that this initial phase of the overall program would result in a finalized set of procedures which would detail the combustion test methods, sampling techniques and analytical procedures for all future evaluations of synfuel combustion characteristics. Procedures that failed to produce satisfactory results were to be modified or replaced as the program progressed.

2.1 EXPERIMENTAL APPARATUS AND APPROACH

The experiments were conducted by EPA in a commercially available package boiler and diesel engine located at their facility in Research Triangle Park, NC. All experiments were conducted at a fixed input or output for each of the two combustion devices. In the package boiler a heat input rate of 740 kW (2.5×10^6 Btu/hr) was used. For the diesel engine an output of 190 kW (250 hp) was used. Both units were operated to produce optimum stack conditions, i.e., minimal smoke. A two hour test period was used for each test fuel. During this test period gaseous samples of the combustion products were monitored continually for O_2, CO, CO_2, NO/NO_x and SO_2. A modified Method 5 particulate sample train was used to obtain organic samples as well as particulate samples. The modification consisted of the addition of a XAD-2 module between the Method 5 filter and impingers to collect condensible organic vapors. The particulate samples were analyzed by Level 1 procedures, with an emphasis on organics.

2.2 RESULTS

The particulate samples collected and analyzed by EPA showed inconsistent particulate loadings for the package boiler and very consistent particulate loadings for the diesel engine. Chemical analyses showed high levels of contamination due to silicon compounds in the package boiler emissions and the same contaminants to a lessor degree in the diesel engine emission.

Speciation, by class, of the organic compounds in the particulate samples resulted in a high percent being identified in the diesel engine samples, and a low-to-high percent being identified in the package boiler samples. No biological tests were conducted due to the low amount of particulate collected.

2.3 CONCLUSIONS

The objective of the Phase I program was only partially satisfied. The test procedures employed by EPA yielded inconsistent results, especially the particulate loading for the package boiler. In addition, only the fuels were subject to an inorganic analysis, while insufficient particulate material was collected to perform any bioassays.

A complete review was made of the test procedures and results at a workshop conducted at the conclusion of the Phase I program. The main conclusions reached at the workshop were:

- Chemical analysis of the Phase I study were not sufficiently discriminatory to determine a difference between the emissions from petrofuels and their synfuel counterparts.
- Boiler data indicated that the operating conditions selected for Phase I testing provided good combustion efficiency over a wide range of fuels.
- A need for better control of key independent operating variables was indicated.
- The fuel pumped to the package boiler should be heated to produce the viscosity for which the burner was designed.

Subsequent evaluation by KVB of the package boiler test procedures determined the following conclusion in addition to the above:

- A significant amount of in-leakage to the package boiler combined with low stack velocity and flow stratification were responsible for the erratic particulate loadings found on this test unit.

2.4 RECOMMENDATIONS

The recommendations from the workshop proceedings were as follows:

- Consider the use of a cytotoxic bioassay such as the rabbit alveolar macrophage (RAM) test as an additional measure of biological response.

- Consider running the package boiler at off-optimum operating conditions which should simulate field operating conditions of similar sized boilers that are poorly maintained and operated.

- Analyze future combustion samples using procedures that can identify specific nitro-organic or polycyclic organic compounds which are known to have greater mutagenic potency.

- Consider sampling a greater fraction of the stack gases by using larger filters, by using more filters in parallel, or by designing a new sampling system that can collect exhaust samples at a faster rate.

- Consider installation of a CO monitor/alarm in the combustion laboratory.

- Consider the use of a fuel spiked with Diisopropylnaphtalene (DIPN) to determine if carryover from one run to the next is significant, while following the usual Phase I cleaning procedure between runs.

- Investigate the use of a Polynuclear Aromatic (PNA) versus excess-oxygen graph as an alternate method of setting optimum boiler operating conditions.

- Take a fuel sample for analysis either the same day as the test, or a day or two ahead.

- Consider the use of chemical compound classification systems such as Paraffin-Olifin-Napthines-Aromatics (PONA) or Saturates Aromatics Resins Alafotics (SARA) as alternatives to IERL-RTP's present system.

- Consider the use of the measurement of Polynuclear Aromatic Hydrocarbons (PAH) (or PNA) quantitatively as a basis for detecting differences in emissions.

- Perform additional studies to determine the range of emissions from a wider range of petrofuels.

- Investigate the possibility of some collaborative tests with EPRI in their upcoming large scale tests with EDS fuels.

- Eliminate siloxanes and phthalates from the samples where possible.

- Provide additional engineering guidance to the statistician to assist in deriving more powerful modeling tools; i.e., for identifying independent, dependent, and interdependent variables.

- Reduce the replication variability by better control of key independent operating variables, e.g., fuel injection temperature, air atomization pressure, and excess air.

In addition to the workshop recommendations, the following recommendations are merited:

- In addition to off-optimum operating test conditions, selected optimum operating test conditions should also be evaluated.

- On <u>any</u> future emission evaluation, in-leakage to the exhaust stack that would influence the particulate mass flow distributions or concentrations must be eliminated. Sampling of the stack to determine uniformity in stack oxygen concentration and flow velocity is mandatory.

SECTION 3.0

COMBUSTION SYSTEMS AND INSTRUMENTATION

Two combustion systems, a package boiler and a diesel engine, were used in the test program. The same gaseous emission instrumentation and particulate collection systems were used for both combustion systems. A description of each system follows.

3.1 PACKAGE BOILER

The boiler used for the package boiler experiments was a commercially available, three-pass, firetube boiler manufactured by North American (NA) and having a thermal input rating of 740 kW (2.5×10^6 Btu/hr). The boiler, shown schematically in Figure 3-1, is located at the Environmental Research Center in Research Triangle Park, NC.

The combustion air was delivered to the system by a fan integral to the burner. The combustion air was modulated by a shutter arrangement also directly connected to the burner. This arrangement is typical of North American burners with firing rates up to at least 17.6 MW (60×10^6 Btu/hr).

The oil atomizer was a standard NA design using air as the atomizing medium. The atomizing air was obtained from the facility compressed air supply and was regulated down from the 10.1 MPa (100 psig) supply pressure to about 2.84 MPa (28 psig) at the burner.

The liquid fuels were drawn from 208 dm^3 (55 gallon) drums located in the oil handling building and delivered to the burner by a gear pump. During those tests where heating of the fuel was necessary, preliminary heating was accomplished by drum heaters, final heating and temperature control was accomplished with the package boiler oil heater. The fuel flow rate was determined by pre-calculating the required meter reading to be set for each fuel and viscosity.

Other than the fuel flow rate, no other flow measurements into or out of the system were made.

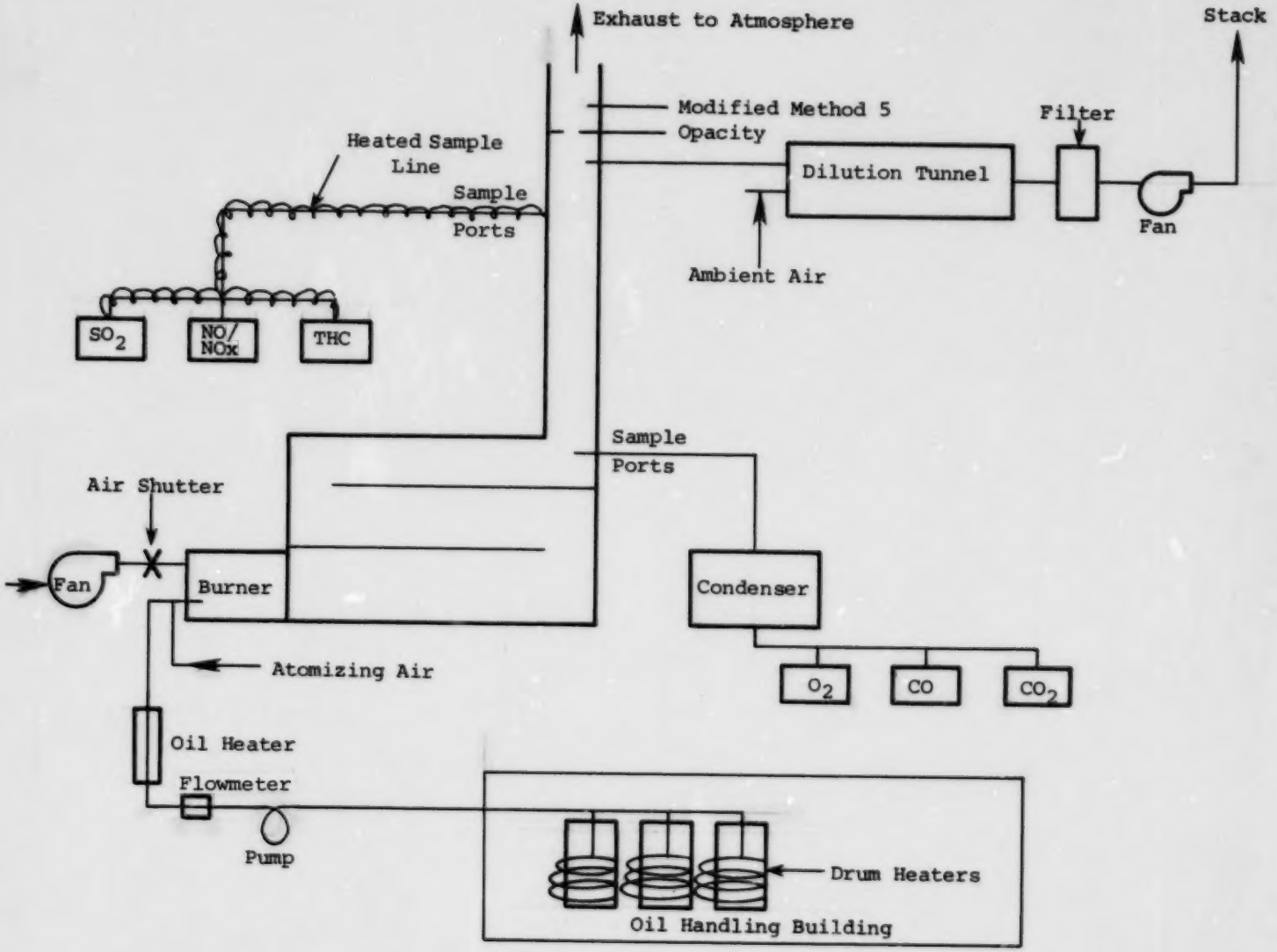


Figure 3-1. Schematic Diagram of the Package Boiler Facility

3.2 DIESEL ENGINE

The engine used in the experiments was a Model D-334 Caterpillar diesel. Currently this model is considered as obsolete but is still in use in many installations. The pertinent diesel engine characteristics are:

- 6-cylinder in-line
- 10.5 liter displacement (638 in^3)
- 1800 RPM
- Turbocharged
- Aftercooled
- Pre-combustion chamber

The diesel engine system is shown schematically in Figure 3-2.

The fuel system was set up to feed from 208 dm^3 (55 gallon) drums mounted horizontally on a barrel transporter. The base oil drum was filled prior to each test run and separate drums were used for each test fuel.

The diesel engine was attached to an electric generator and the diesel engine load was set by adjusting the desired loading in kilowatts. This load was held constant during the test runs at a value equal to approximately 80 percent of the electric generators capacity (80 kW)

3.3 INSTRUMENTATION

As previously mentioned, none of the air flows supplied to either combustion device were measured. All temperature measurements were made using chromel-alumel thermocouples. The measurements of primary interest were the gaseous and particulate emissions at the various locations as shown in Figures 3-1 and 3-2. A very detailed description of both test facilities and the instrumentation used was prepared as part of the data package for the workshop described in Reference 13.

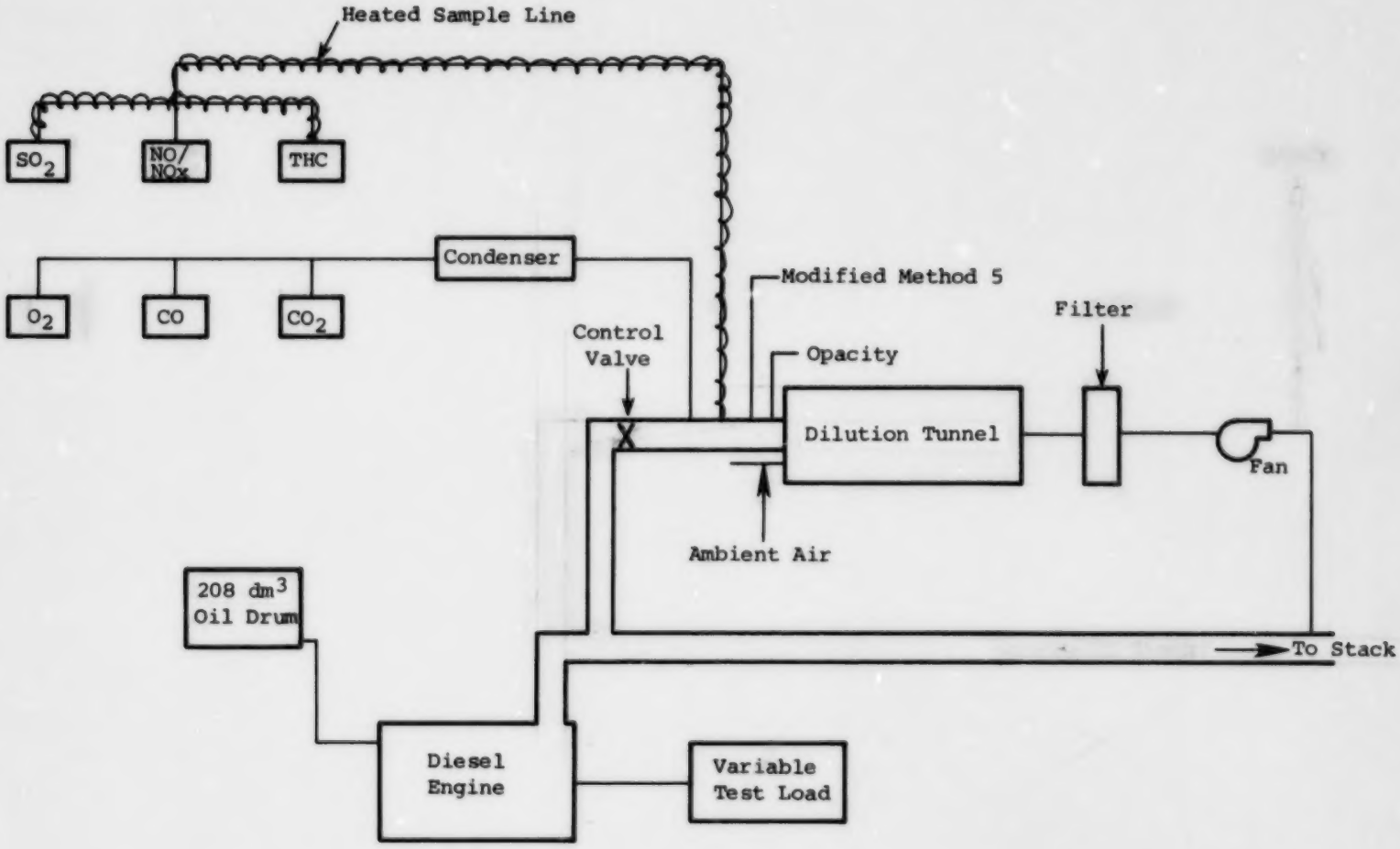


Figure 3-2. Schematic Diagram of the Diesel Engine Facility

3.3.1 Gaseous Emissions Measurements

Continuous gas analyzers were used to measure O_2, NO/NO_x, CO, CO_2, THC and SO_2. A summary of the gas analysis instrumentation is presented in Table 3-1. The gaseous emissions were taken at the locations indicated in Figure 3-1 and 3-2. The SO_2, THC and NO/NO_x samples were obtained by transporting "wet" gas samples to the respective analyzers through heated teflon sample lines. A detailed description of the calibration procedures and operating procedures for the continuous analyzers is given in Appendix B.

TABLE 3-1. CONTINUOUS GASEOUS EMISSION ANALYZERS

Species	Analyzer
NO/NO_x	Thermo Electron Model 10A chemiluminescent
O_2	Beckman Model 755 Paramagnetic
CO	Beckman Model 865 NDIR
CO_2	Beckman Model 865 NDIR
THC	Scott Model 415 Flame Ionization
SO_2	Thermo Electron Series 40 Pulsed Fluorescence

3.3.2 Particulate Emission Measurements

Smoke Spots were measured using a standard Bacharach smoke spot test with a R.A.C. reflectometer. Particulate samples were obtained at the locations indicated in Figures 3-1 and 3-2.

A modified Method 5 train was used to obtain a sample of the stack gas. This train used an XAD-2 module organic adsorber with an integral sample gas conditioner in addition to the normal particulate cyclone, filter and impinger train. Large quantities of particulate matter were obtained by a filter located downstream of the dilution tunnel. This filter was intended to trap all solid particulate plus condensibles found at the temperatures exiting the dilution tunnel (~314 K -- ~105°F). A detailed set of procedures for use of the filter and the modified Method 5 train is given in Appendix B.

3.4 TEST PROCEDURES

3.4.1 Package Boiler

The package boiler was cleaned as completely as possible before each test run both by brushing and vacuuming. The boiler was then "reconditioned" by firing No. 2 fuel oil for an hour before each test run. This procedure also brought the boiler to operating temperature. At this time the burner was shut down and all fuel passages were flushed with the fuel to be tested. The boiler was then fired on the test fuel with the oil flow rate set to a pre-calculated value for the test fuel, the atomizing air was set and the boiler stabilized at 417 to 422 K (290 to 300°F) stack temperature.

A curve of Bacharach smoke number versus percent excess air was then defined from which the desired excess air condition was determined for the set point for particulate sampling. This point was chosen to provide optimum boiler operating conditions (i.e., low smoke number), thus, the excess air for each fuel tested was different. The range of excess air varied from as low as 9.3 percent on No. 2 oil to as high as 26.5 percent on No. 6 oil. The excess air was based on the measured stack oxygen concentration.

Each particulate test was run for two hours. During this period of time the continuous gaseous analyzers were in operation and a modified Method 5 sample was taken, as well as the collection of a particulate sample at the dilution tunnel exit.

At the end of the test period the boiler was shut down and the fuel lines were flushed with No. 2 oil and the entire sequence was reinitiated.

3.4.2 Diesel Engine

The diesel engine fuel system was set up to feed from a 208 dm^3 (55 gallon) drum mounted on a horizontal transporter. The engine was started and allowed to idle during warm up. The speed was then advanced to a fast idle and the load bank was turned on and the desired loading in kilowatts was set where it remained until steady state was reached. Once steady state was achieved, the load was removed and the engine was switched to the test fuel

barrel. After switching fuels, the desired load was reapplied and the test sample was taken. After sample collection was complete, the load was removed and the engine was switched to operate on No. 2 oil to purge the system.

As with the package boiler, the continuous analyzers were in operation during the sample period and a modified Method 5 sample was taken as well as the collection of a particulate sample at the dilution tunnel exit.

3.4.3 Dilution Tunnel Operation

The set-up for both combustion systems was essentially the same, the primary difference in operation was that for the package boiler only a small portion of the flue gas was drawn through the dilution tunnel, whereas for the diesel engine test nearly all the flue gas was drawn through the dilution tunnel.

The dilution tunnel was cleaned by brushing and vacuuming with some areas being cleaned with rags after each test run. After cleaning, the unit was reassembled and leak checked.

Two laminar flow meters (Meriam model 50MC2) measured the flow rate of dilution air plus flue gas leaving the tunnel and the flow rate of dilution air being drawn into the tunnel. The dilution air flow was approximately nine times the volume flow of the flue gas thus yielding a volume dilution ratio of ~ 9 to 1.

3.5 ANALYTICAL CHEMISTRY PROCEDURES

3.5.1 Sampling Methods

The samples collected for analysis were obtained as described in Section 3.3.2. This sampling procedure provided the following samples to be analyzed from both the package boiler and the diesel engine tests:

- Modified Method 5 (MM5) train
  XAD-2 sorbent resin
  Filter (MM5)
  Probe rinse
  Organic module condensate

- Dilution tunnel filter

3.5.2 Analysis Procedures and Criteria

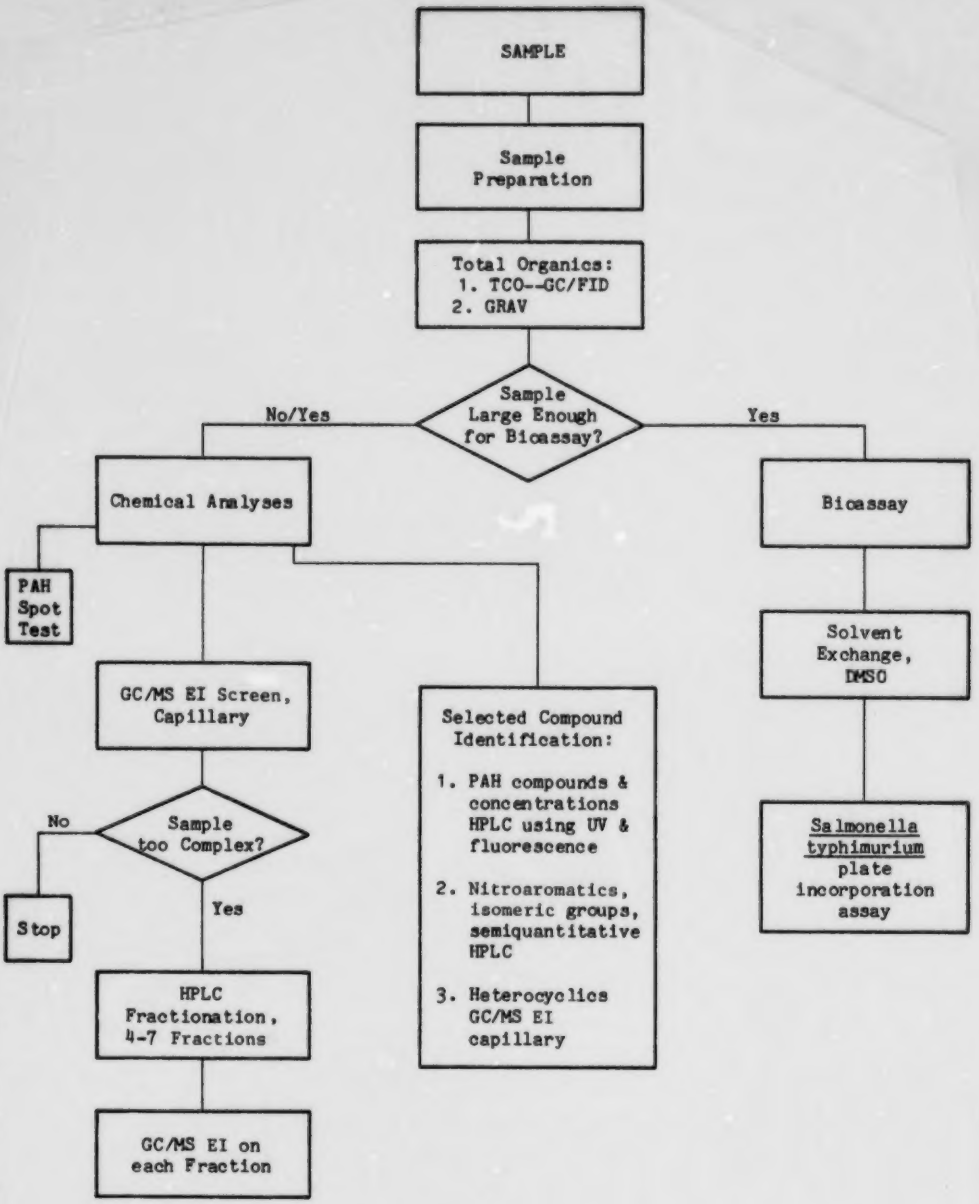
A detailed description of the analytical procedures is given in Appendix B. A summary of the tests performed and the method of analysis is given in Table 3-2 and Figure 3-3.

TABLE 3-2. CHEMICAL/ORGANIC ANALYSES

Species	Method	Modified Method 5 Train				Dilution Tunnel
		XAD-2	Filter	Probe Rinse	Condensate	Filter
Inorganic*	--					
Organic						
Mass gravimetric	Weigh		x			x
Fraction mass, TCO†	GC/FID	x			x	
Fraction mass, Grav†	Weigh	x	x	x	x	x
PAH Spot Test		x			x	x
Compounds in Fractions†	HPLC	x				x

*Performed on fuels only (See Section 4)

†Level 1 analysis



LEGEND:

TCO, GRAV	-- Total Chromatographable Organics
GC/FID	-- Gas Chromatograph with a Flame Ionization Detector
PAH	-- Polynuclear Aromatic Hydrocarbon
GC/MS EI	-- Gas Chromatograph/Mass Spectrograph with Electron Impact
HPLC	-- High Performance Liquid Chromatograph
DMSO	-- Dimethylsulphoxide

Figure 3-3. Organic Emissions Analytical Flow Scheme

SECTION 4.0

FUEL CHARACTERISTICS

A total of six petrofuels and four synfuels were used in the Phase I test program. A summary of the fuels used and the nominal physical and chemical properties of each is given in Table 4-1. It is recognized that there are some questionable values reported in this table, in particular the nitrogen values. At the issuance of this report these questionable values have not been resolved, however, many of these same fuels will be used in Phase II by which time the discrepancies will be resolved and subsequently reported.

The No. 6 fuel oils (except the high nitrogen No. 6 oil) were blended for this program to provide the range of sulfur values shown. The same base oil was used to do this blending.

The derivation and subsequent processing of the synfuels is not known. These particular oils were procured for this program but the exact origin of the fuels was not traceable. Much higher percentages of nitrogen and sulfur than reported in Table 4-1 were found for an EDS fuel in a previous combustion test (14) which indicates that hydrotreating was done to the EDS fuel used in these tests.

The test fuels were subjected to some of the same analytical chemistry methods that were used on the captured combustion particulate samples. Table 4-2 compares organic components and the PAH contents for each fuel. This table shows the SRC-II heavy distillate to have quite high PAH levels compared to the other fuels. As expected, the methanol showed a negative indication to the PAH spot test.

Class identification of the organic material in the fuels is compared in Table 4-3. Of note in Table 4-3 are the relatively low percentages of organics that were identified for all three of the No. 6 fuel oils.

TABLE 4-1. REPORT OF FUEL OIL TESTS

	No. 2 In-House	No. 2 In Barrels	No. 6 1.4% Sulfur	No. 6 2.1% Sulfur	No. 6 2.9% Sulfur	No. 6 0.7% Nitrogen	Methanol	Shale Derived No. 2	EDS Middle Distillate	SRC-II Heavy Distillate
BTU/lb										
Gross	19,364	19,408	18,984	18,438	18,181	18,735	9,104	19,694	18,574	16,708
Net	-	18,300	17,930	17,453	17,369	17,689	7,968	18,489	17,654	16,022
BTU/gal										
Gross	138,182	138,922	143,120	147,209	152,611	-	60,359	137,050	146,010	148,618
Net	-	130,991	135,174	139,345	145,795	-	52,828	128,665	138,778	142,516
Specific gravity @ 60/60°F by pycnometer	0.8571[a]	0.8600	0.9052	0.9589	1.0082	0.9254	0.7971	0.8355	0.9443	1.0681
Density[a] @ 60°F	0.8562	0.8592	0.9043	0.9580	1.0072	0.9245	0.7955	0.8347	0.9434	1.0671
API gravity @ 60°F	33.6	33.0	24.8	16.1	8.8	21.4	46.0	38.0	18.3	0.98
Density[a] @ 100°F	0.8441	0.8599	0.8902	0.9467	0.9930	0.9129	0.7754	0.8192	0.9279	1.0534
Density[a] @ 210°F	0.8405	0.8590	0.8503	0.9018	0.9565	b	-	0.7774	0.8849	1.0114
Viscosity @ 100°F, cs	2.75	2.64	21.93	1,396	891.3[c]	b	0.62	2.79	3.37	52.70
Viscosity @ 210°F, cs	1.14	1.09	4.53	40.6	39.5	b	-	1.14	1.24	3.60
KF water, wt. %	-	0.01	0.37	2.26	1.33	1.04	0.11	0.03	0.11	2.70
Ash, wt. %	<0.01	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Carbon, wt. %	87.0	85.66	83.23	83.59	86.04	86.23[d]	36.32	84.42	84.66	86.01[d]
Hydrogen, wt. %	12.5	12.15	11.55	10.80	9.90	11.47[d]	12.45	13.21	10.08	7.52[d]
Nitrogen, wt. %	<0.01	0.012	0.028	0.079	0.096	0.27[d]	0.022	0.013	0.080	0.96[d]
Sulfur[e], wt. %	0.22	0.17	1.44	2.43	2.75	0.89[d]	<5 ppm[f]	<5 ppm[f]	0.01	0.55[d]

[a]Calculated value.

[b]The density at 210°F from which viscosity is derived apparently was affected by a component which was volatile at 210°F. Variable results for density were obtained, e.g.,

Run	Density @ 210°F
1	0.9007
2	0.9074
3	0.9049

[c]The sample was observed to contain free water. This could affect the report viscosity.

[d]M. Cooke, and A. Wencky, "Comparative Fuels Analysis," Battelle Columbus Laboratories, Columbus, Ohio, Contract No. 68-02-3628, Work Assignment 010, Draft Report to U.S. EPA, IERL, Research Triangle Park, North Carolina, April 1982.

[e]Bomb method.

[f]ppm by weight.

TABLE 4-2. FUEL TCO, GRAV, AND PAH SPOT TEST ANALYSIS

Fuel	TCO[a] Concentration mg/mL	GRAV[b] Analysis mg/mL	Total (TCO + GRAV) mg/mL	PAH	
				Spot Test	Concentration mg/mL
No. 2, In-House	729	240	969	positive	2 - 20
No. 2, In Barrels	685	200	885	positive	20 - 200
No. 6, 1.4% S	433	646	1 079	positive	20 - 200
No. 6, 2.1% S	241	791	1 032	positive	20 - 200
No. 6, 2.9% S	80	1 008	1 088	positive	200 - 2 000
No. 6, 0.7% N	40	923	963	positive	20 - 200
Methanol	3.8	0	3.8	negative	-
Shale Derived No. 2	753	394	1 147	positive	0.2 - 2.0
EDS Middle Distillate	741	248	989	positive	2 000
SRC-II Heavy Distillate	255	892	1 147	positive	20 000

[a]TCO - Total Chromatographable Organics. Materials having boiling points in the range of 100°C to 300°C. See Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht," IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Research Triangle Institute, Research Triangle Park, N.C., EPA-600/7-78-201, October 1978.

[b]GRAV - Gravimetric Analysis. See Reference in footnote "a."

TABLE 4-3. ORGANIC CLASS COMPARISON -- FUELS

Fuels	No. 2 In-House mg/mL	No. 2 In Barrels mg/mL	No. 6 1.4% S mg/mL	No. 6 2.1% S mg/mL	No. 6 2.9% S mg/mL	Shale Derived No. 2 mg/mL	EDS Middle Distillate mg/mL	SRC-II Heavy Distillate mg/mL
Aliphatic Hydrocarbons								
Alkanes	376	333	152	95	-	441	54	-
Alkenes	8.4	9.8	38	5.5	-	172	-	-
Nitrogen Containing	-	-	0.33	-	-	-	-	-
Aromatic Hydrocarbons	41	36	18	-	23	15	158	149
PAH Hydrocarbons								
MW < 216	159	160	103	7.8	30	-	51	292
MW > 216	-	-	-	-	3.9	-	-	25
Aldehydes	21	17	-	-		-	6.7	-
Heterocyclic Oxygen	-	-	-	-	-	-	30	42
Alcohols								
R-OH	-	-	2.5	10	-	-	16	-
Aromatic	-	-	-	-	-	-	40	-
Phenols								
Alkyl	-	-	-	-	-	-	13	-
Ketones	-	-	-	0.34	-	14	128	90
Amines								
Aliphatic	5.8	4.6	-	9.2	-	3.6	-	3.5
Heterocyclic Nitrogen	-	-	-	-	-	-	52	44
Indoles	-	-	-	-	-	-	57	-
Quinolines	-	-	-	-	-	33	-	-
Heterocyclic Sulfur	-	-	11	-	-	-	-	-
Benzothiophenes	-	-	-	-	-	-	-	83
Mixed Functionality (list)								
Heterocyclic (N&S)	-	-	-	-	-	-	-	18
Heterocyclic (N&O)	-	-	-	-	-	-	-	30
Total Identified Organic	611	560	324	128	57	679	606	777
Total Extractable Organic	969	885	1 079	1 032	1 088	1 147	989	1 147
Percent Identified	63	63	30	12	5.2	59	61	68

Finally, a trace elemental analysis of the fuels was made and is given in Table 4-4. For those fuels containing sulfur, that element is shown to be a major component. The list of elements was restricted to the ten largest mass fractions found for each fuel.

TABLE 4-4. FUEL ELEMENTAL ANALYSES
µg/ml

Element	No. 2 Fuel In Barrels	No. 6 1.4%S	No. 6 2.1%S	No. 6 2.9%S	Methanol	Shale Derived No. 2	EDS Middle Distillate	SRC-II Heavy Distillate
F	2.4	20	380	1700		2.87		
Na	1.02	12	210	1200				63
Mg	7.98	14				65.8	8.6	
Al		13		600		3.01	11	
Si	9.25	21	460	780		34.2	87	70
P				1000				130
S	34.8	Major	Major	Major		1.56	3.7	330
Cl								140
K							2.7	
Ca			160				2.7	150
Sc				604				
Ti			290					
V		900	380	6040			75	
Mn								31
Fe		20	280	1500				1500
Ni	2.9	49	220			11	43	130
Cu	1.64							120
Zn			870	4900				
Ge						1.17		
Se		26						
Rb						0.713		
Mo						1.12		
Sb	0.957				8	0.821	2.1	
Cs					0.74			
Ba					1		1	
Gd					2			
Ta	1.02							
W					0.9			
Os	0.905				2			
Ir					2			
Pt					1			
Au					0.7			
Pb					1			

SECTION 5.0

PHASE I - EXPERIMENTAL RESULTS AND DISCUSSION

Twenty-five test runs were made during the program. Twenty of the runs were made on the package boiler, but only fifteen of the runs produced particulate samples. Five runs were made on the diesel engine. A summary of the run numbers, test fuels, smoke numbers and measured stack oxygen (O_2) concentrations are given in Table 5-1. Seven random replicate test runs were made and in all of the data tables these replicate runs are paired for ease of comparison.

5.1 COMBUSTION SYSTEM PERFORMANCE

5.1.1 Package Boiler

A. Gaseous Emissions--

The gaseous emission data collected for all of the test runs are summarized in Table 5-2. Since only the fuel flow was measured and not the air flow, the validity of the data cannot be easily checked. Had air flow been measured the stack oxygen could be checked against the calculated stack oxygen based upon air flow, fuel flow and fuel composition. It is possible, however, to check the measured SO_2 values since in most combustion systems 95 to 100 percent of the fuel sulfur is converted to SO_2. When this comparison is made, the result is as shown in Figure 5-1. KVB calculated the SO_2 concentration using the fuel elemental analysis (including the sulfur content) at the O_2 level measured by EPA. This figure shows a large discrepancy between the calculated and measured values at a given stack O_2. The SO_2 concentrations measured by EPA were, on the average, 29 percent less than those calculated from the elemental composition and stack O_2. Since the measured values are lower than the calculated values, this could indicate either a leak in the sample system, a bad calibration gas (or calibration procedure), or a large leakage of air flow into the exhaust stack between the oxygen sample port and the SO_2 sample port. Further analysis of this data and the determination of the reason for the above discrepancy are not possible from the available data.

TABLE 5-1. SUMMARY OF TESTS

Run No.	Fuel	Measured Stack O_2 Vol Pct, Dry	Smoke No.
Package Boiler			
1R	No. 2, In-house	2.1	3.0
16	No. 2, In-house	2.4	1.0
3	No. 2, In Barrels	1.9	1.8
9	No. 6, 1.4% S	2.9	4.5
14	No. 6, 1.4% S	2.8	5.0
7R	No. 6, 2.1% S	4.2	5.0
12	No. 6, 2.1% S	4.7	5.0
8	No. 6, 2.9% S	4.3	4.5
10R	No. 6, 0.7% N	2.9	3.0
4R	Methanol	1.7	0
6	Shale Derived No. 2	2.1	3.0
5	EDS Middle Distillate	2.8	2.1
11R	EDS Middle Distillate	2.8	3.0
13	SRC-II Heavy Distillate	2.7	2.0
15	SRC-II Heavy Distillate	2.7	1.2
Diesel Engine			
1	No. 2, In-house	10.0	2.5
5	No. 2, In-house	10.1	1.0
3	No. 2, In Barrels	9.8	1.0
2	Shale Derived No. 2	10.1	1.0
4	Shale Derived No. 2	10.2	1.0

TABLE 5-2. AS-MEASURED PACKAGE BOILER EXHAUST GAS STACK EMISSIONS

Run No.	Fuel	O_2 Pct(1)	CO_2 Pct(1)	CO ppm(2)	NO ppm(3)	NO_x ppm(3)	THC ppm(3)	SO_2 ppm(3)
1R	No. 2, In-house	2.1	13.6	10	59	59	1.0	89
16	No. 2, In-house	2.4	13.6	10	70	70	1.5	84
3	No. 2, In Barrels	1.9	14.0	15	66	66	1.0	89
9	No. 6, 1.4% S	2.9	13.2	15	159	159	3.0	540
14	No. 6, 1.4% S	2.8	13.8	25	150	150	1.5	554
7R	No. 6, 2.1% S	4.2	12.7	2	212	212	2.0	900
12	No. 6, 2.1% S	4.7	12.1	20	205	205	1.0	825
8	No. 6, 2.9% S	4.3	12.6	15	190	190	5.0	1150
10R	No. 6, 0.7% N	2.9	13.7	15	275	275	2.0	356
4R	Methanol	1.7	13.5	15	35	35	1.0	4
6	Shale Derived No. 2	2.1	13.5	10	63	63	1.0	2
5	EDS Middle Distillate	2.8	13.7	13	100	100	1.0	6
11R	EDS Middle Distillate	2.8	14.0	10	100	100	0.75	8
13	SRC-II Heavy Distillate	2.7	14.9	10	360	360	1.0	231
15	SRC-II Heavy Distillate	2.7	15.0	15	375	375	3.0	227

(1) Percent Volume Dry

(2) Parts Per Million Volume Dry

(3) Parts Per Million Volume Wet

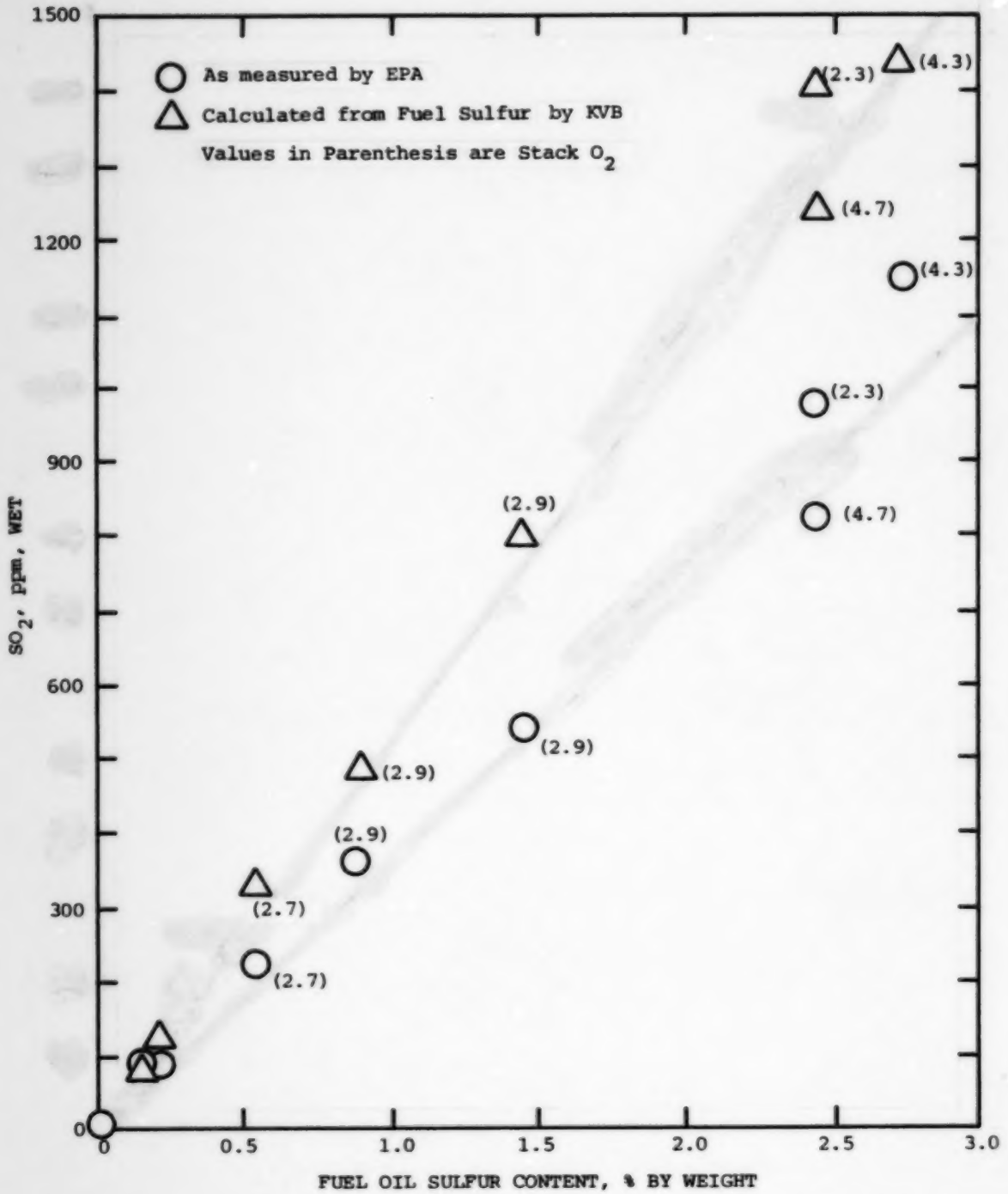


Figure 5-1. SO_2 Emissions Comparison for Package Boiler

B. Particulate Emissions Measurements--

Flue gas particle concentrations were determined at two locations, in the exhaust stack and at the dilution tunnel exit. A tabulation of these data is given in Table 5-3. The measured dilution tunnel particulate loading (mg) was normalized by the measured flue gas volume (m^3) entering the dilution tunnel. This would allow the stack particulate concentration (mg/m^3) and the dilution tunnel particulate concentration to be compared directly. These data, in general, show poor agreement between the particulate concentrations measured at these two locations. On the average, the modified Method 5 concentration exceeded the dilution tunnel concentration by a factor of 2.

The discrepancies shown in Table 5-3 were fully discussed during the workshop without a total explanation as to the cause. Subsequent investigations into the boiler's operating characteristics have identified the probable cause of this discrepancy. Variable air leakage into the exhaust stack combined with stratified flow in the stack have been identified as the probable causes of the variations observed for the Phase I tests. Both air leakage and flow stratification could affect the concentrations of particulate drawn into both the dilution tunnel and the modified Method 5 train. The cause of the air leakage was due to an undampered stack permitting a negative draft in the stack. The flow stratification was due to a combination of low exhaust gas velocity (~2.4 m/s, ~8 ft/sec) and an offset in the stack to clear a roof structural member.

5.1.2 Diesel Engine

A. Gaseous Emissions--

The gaseous emission data collected for all test runs with the diesel engine are summarized in Table 5-4. Engine operation was completely satisfactory on all fuels used. No operational or hardware changes were required. These data are very consistent for all test runs. A discrepancy in the measured SO_2 levels and the SO_2 levels calculated based on 100 percent conversion of the fuel sulfur to SO_2 also exists for these diesel engine tests. This SO_2 discrepancy thus appears to be due in part to a sampling problem either in the calibration gas, the sampling procedures or fuel analysis.

TABLE 5-3. PACKAGE BOILER EXHAUST GAS PARTICULATE SUMMARY

Run No.	Fuel	Modified Method 5 Sample Train Loading			Dilution Tunnel	
		Probe Wash mg	Filter mg	Concentration[1] mg/m^3	Loading mg	Concentration mg/m^3
1R	No. 2, In-house	3.9	4.3	2.81	78.0	1.25
16	No. 2, In-house	7.1	0.2	1.42	133.0	1.06
3	No. 2, In Barrels	2.6	6.7	3.68	97.6	1.64
9	No. 6, 1.4% S	2.6	126.9	62.9	3501.2	58.9
14	No. 6, 1.4% S	38.6	191.3	120.0	3314.4	46.0
7R	No. 6, 2.1% S	127.8	746.5	367.0	7580.7	135.3
12	No. 6, 2.1% S	210.2	344.8	276.0	11293	219.3
8	No. 6, 2.9% S	224.9	385.9	257.0	6306.1	130.0
10R	No. 6, 0.7% N	12.6	52.5	32.4	686.7	9.73
4R	Methanol	2.6	3.6	2.18	33.1	0.538
6	Shale Derived No. 2	0.5	183.0	43.7	183.0	2.98
5	EDS Middle Distillate	51.6	366.8	146.0	95.0	1.32
11R	EDS Middle Distillate	5.6	135.4	67.1	238.6	5.47
13	SRC-II Heavy Distillate	18.4	393.3	206.0	329.6	7.31
15	SRC-II Heavy Distillate	0.0	12.8	6.40	305.0	6.57

[1]Particulate concentration includes probe rinse, cyclone and filter loadings.

TABLE 5-4. AS-MEASURED DIESEL ENGINE EXHAUST GAS STACK EMISSIONS

Run No.	Fuel	O_2 Pct(1)	CO_2 Pct(1)	CO ppm(2)	NO ppm(3)	NO_x ppm(3)	THC ppm(3)	SO_2 ppm(3)
1	No. 2, In-house	10.0	8.3	62	485	485	3.0	52
5	No. 2, In-house	10.1	8.2	80	565	565	7.0	40
3	No. 2, In Barrels	9.8	8.3	68	575	575	4.5	40
2	Shale Derived No. 2	10.1	8.0	50	530	530	4.5	0
4	Shale Derived No. 2	10.2	8.0	75	470	470	7.0	0

(1) Percent Volume Dry

(2) Parts Per Million Volume Dry

(3) Parts Per Million Volume Wet

B. Particulate Emissions Measurements--

The flue gas particulate concentrations were determined at two locations; at the exhaust stack and at the dilution tunnel exit. A tabulation of these data are given in Table 5-5. Again, the measured dilution tunnel filter loadings were normalized with respect to the measured flue gas drawn into the dilution tunnel. These data show good agreement for the two locations which is in sharp contrast to the package boiler results. This is an important result, because it shows that a large sample, as collected on the dilution tunnel exit filter, and as required for the bioassay, can be obtained if a representative flue gas sample can be supplied to the dilution tunnel.

The good comparison between the particulate samples from the diesel tests also supports the conclusion that the problem with the package boiler data is probably due to a different concentration of particulate matter being drawn into the modified Method 5 sample train than is drawn into the dilution tunnel from the source in the stack.

5.2 ANALYTICAL CHEMISTRY RESULTS

Test samples from both the package boiler and the diesel engine tests were analyzed for organics using the procedures summarized in Section 3.5.2 and outlined in Appendix B. No inorganic analyses of the particulate samples was performed.

Flue gas organic concentrations from the package boiler tests are given in Tables 5-6 and 5-7. It was found from the data shown in Table 5-7 that a large percentage of the sample was due to contaminants (silicones, phthalates and solvents). The possible source of one of the contaminants, silicone, was a sealing compound used on the boiler after each cleaning operation. This use of silicone sealing compounds was stopped as soon as it was identified that silicone was a contaminant of the particulate samples. The corrected values with the contaminants removed is given in Table 5-8.

The results of the organic analysis for the diesel engine tests are given in Tables 5-9 and 5-10. Similarly, as for the package boiler results, corrected organic levels with the contaminants removed are given in Table 5-11.

TABLE 5-5. DIESEL ENGINE EXHAUST GAS PARTICULATE SUMMARY

Run No.	Fuel	Modified Method 5 Sample Train Loading Probe Wash mg	Modified Method 5 Sample Train Loading Filter mg	Modified Method 5 Sample Train Concentration[1] mg/m^3	Dilution Tunnel Loading mg	Dilution Tunnel Concentration mg/m^3
1	No. 2, In-house	9.0	24.5	18.5	924.0	17.1
5	No. 2, In-house	3.6	44.5	27.1	1464.2	28.2
3	No. 2, In Barrels	6.8	41.6	27.5	1487.0	27.8
2	Shale Derived No. 2	15.2	23.4	21.7	969.1	19.0
4	Shale Derived No. 2	38.2	21.5	33.5	1046.1	19.6

[1]Particulate concentration includes probe rinse, cyclone and filter loadings.

TABLE 5-6. DILUTION TUNNEL ORGANIC COMPONENTS -- PACKAGE BOILER

Run No.	Fuel	TCO[a] mg	GRAV[b] mg	Total (TCO+GRAV) mg	TCO[c] Concentration mg/m^3	GRAV[d] Concentration mg/m^3	Diluted Organic Concentration[e] mg/m^3	Flue Gas Organic Concentration[d] mg/m^3
1R	No. 2, In-House	0.294	3.20	3.49	0.000466	0.00507	0.00553	0.0561
16	No. 2, In-House	0.488	0	0.488	0.000304	0	0.000304	0.00389
3	No. 2, In Barrels	0.437	13.6	14.0	0.000699	0.0217	0.0224	0.235
9	No. 6, 1.4% S	0.673	1.3	1.97	0.001079	0.00208	0.00316	0.0332
14	No. 6, 1.4% S	0.143	0	0.143	0.000221	0	0.000221	0.00198
7R	No. 6, 2.1% S	0.785	6.1	6.89	0.00125	0.00972	0.0110	0.123
12	No. 6, 2.1% S	(lost)	0	>0	>0	>0	>0	>0
8	No. 6, 2.9% S	0.634	3.7	4.33	0.00100	0.00685	0.00685	0.0895
10R	No. 6, 0.7% N	0.642	0	0.642	0.00100	0	0.00100	0.00909
4R	Methanol	0.170	5.50	6.67	0.00027	0.00863	0.00890	0.0922
6	Shale Derived No. 2	(lost)	19.2	>19.2	>0	>0.0303	>0	>0.312
5	EDS Middle Distillate	0.514	13.6	14.1	0.000749	0.0198	0.0206	0.196
11R	EDS Middle Distillate	0.681	2.8	3.48	0.00110	0.0045	0.00562	0.0798
13	SRC-II Heavy Distillate	0.586	0	0.586	0.00092	0	0.00092	0.0130
15	SRC-II Heavy Distillate	0.391	2.50	2.89	0.00063	0.00400	0.00463	0.0623

[a] TCO - Total Chromatographable Organics. Materials having boiling points in the range of 100°C to 300°C. See Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht," IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Research Triangle Institute, Research Triangle Park, N.C., EPA-600/7-78-201, October 1978.

[b] GRAV - Gravimetric Analysis.

[c] [(TCO)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[d] [(GRAV)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[e] [(TCO+GRAV)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[f] Material extracted from dilution tunnel filter per standard cubic meter of dry flue gas. Volume corrected to 293.15 K, 101.3250 kPa, dry basis.

TABLE 5-7. MODIFIED METHOD 5 SAMPLE TRAIN ORGANIC COMPONENTS -- PACKAGE BOILER

Run No.	Fuel	XAD-2 Extract TCO[a] mg	XAD-2 Extract GRAV[b] mg	RAC Train Filter GRAV mg	Probe Rinse GRAV mg	Organic Module Condensate TCO mg	Organic Module Condensate GRAV mg	Total (TCO+GRAV) mg	Organic Concentration[c] mg/m^3
1R	No. 2, In-House	1.47	3.40	0.12	0.10	0.140	2.4	7.63	2.61
16	No. 2, In-House	1.56	0	0	-	0.050	0	1.61	0.321
3	No. 2, In Barrels	1.54	0.4	0	0	0.346	4.0	6.29	2.49
9	No. 6, 1.4% S	3.05	2.2	-	0.43	0.214	1.9	7.79	3.78
14	No. 6, 1.4% S	2.69[d]	0	0	2.00	0.405	0	5.10	2.67[d]
7R	No. 6, 2.1% S	1.64	0.45	40.5	0.98	0.307	0.5	44.38	18.6
12	No. 6, 2.1% S	0.361	0	0.36	0.38	2.35	0	3.45	1.72
8	No. 6, 2.9% S	64.5	2.2	3.38	0	0.285	0.8	71.17	29.9
10R	No. 6, 0.7% N	(lost)	0	0	0	0.322	1.8	≥2.12	≥1.05
4R	Methanol	1.62	4.4	0	0.14	0.277	6.8	13.2	4.63
6	Shale Derived No. 2	1.81	1.2	0	-	0	1.15	4.16	0.990
5	EDS Middle Distillate	21.9	2.3	61.2	33.1	0.233	5.2	123.93	43.2
11R	EDS Middle Distillate	0.806	0	0.79	0	0.666	0	2.26	1.08
13	SRC-II Heavy Distillate	4.82	0	0	-	0.851	0	5.67	2.84
15	SRC-II Heavy Distillate	1.41	0	0	-	0.094	0	1.50	0.750

[a] TCO - Total chromatographable organics. Materials having boiling points in the range of 100°C to 300°C. See Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht," IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Research Triangle Institute, Research Triangle Park, N.C., EPA-600/7-78-201, October 1978.

[b] GRAV - Gravimetric Analysis. Chromatographable material having normal boiling points greater than 300°C. Defined in Reference cited in footnote "a."

[c] [(TCO+GRAV)/(st. vol. in m^3, 293.15 K, 101.3240 kPa, dry basis)].

[d] There may have been some sample spilled.

TABLE 5-8. CORRECTED[a] TCO AND GRAV VALUES -- PACKAGE BOILER

Run No.	Fuel	Modified Method 5 Sample Train[b]					Dilution Tunnel					Flue Gas Organic Concentration mg/m³
		Percent Identified	XAD-2 Extract				Percent Identified					
			TCO		GRAV			TCO		GRAV		
			mg	mg/m³	mg	mg/m³		mg	mg/m³	mg	mg/m³	
1R	No. 2, In-House	42	1.02	0.347	1.9	0.67	23	0.294	0.00472	3.2	0.051	0.056
16	No. 2, In-House	56	1.45	0.289	0	0	231	0.488	0.00390	0	0	0.0039
3	No. 2, In Barrels	40	0.902	0.355	0.25	0.10	17	0.437	0.00733	13.6	0.23	0.24
9	No. 6, 1.4% S	26	1.74	0.844	1.8	0.92	58	0.576	0.00968	0.58	0.0098	0.019
14	No. 6, 1.4% S	10	2.69[c]	1.41[c]	0	0	303	0.713	0.00989	0	0	0.0099
7R	No. 6, 2.1% S	4.2	1.58	0.664	0.27	0.12	33	0.658	0.0117	5.5	0.099	0.11
12	No. 6, 2.1% S	3.6	0.361	0.180	0	0	-	(lost)	-	0	0	>0
8	No. 6, 2.9% S	87	4.20	1.80	0.82	0.34	22	0.564	0.0117	3.4	0.070	0.082
10R	No. 6, 0.7% N	-	(lost)	-	-	-	176	0.595	0.00843	0	0	0.0084
4R	Methanol	26	1.16	0.407	3.8	1.3	7.9	0.158	0.00256	5.2	0.084	0.087
6	Shale Derived No. 2	42	1.28	0.303	0.67	0.16	-	(lost)	-	-	-	-
5	EDS Middle Distillate	19	7.50	2.63	2.0	0.71	16	0.514	0.00715	12.6	0.18	0.19
11R	EDS Middle Distillate	17	0.646	0.308	0	0	65	0.645	0.0148	2.8	0.064	0.079
13	SRC-II Heavy Distillate	46	4.82	2.41	0	0	131	0.586	0.0130	0	0	0.013
15	SRC-II Heavy Distillate	97	1.41	0.703	0	0	48	0.391	0.00843	2.1	0.045	0.053

[a]Corrections made for contaminants (silicone, phthalate, and solvent) in identified portions of the extracts.

[b]Includes extracts from XAD-2, probe rinse, RAC train filter, and organic module condensate.

[c]Concentrations uncertain. Sample was spilled during preparation.

TABLE 5-9. DILUTION TUNNEL ORGANIC COMPONENTS -- DIESEL

Run No.	Fuel	TCO[a] mg	GRAV[b] mg	Total (TCO+GRAV) mg	TCO[c] Concentration mg/m^3	GRAV[d] Concentration mg/m^3	Diluted Organic Concentration[e] mg/m^3	Flue Gas Organic Concentration[d] mg/m^3
1	No. 2, In-House	3.36	66.9	70.3	0.00633	0.126	0.132	1.30
5	No. 2, In-House	2.77	107	109.8	0.0047	0.182	0.187	2.11
3	No. 2, In Barrels	7.64	123	130.6	0.0127	0.205	0.218	2.45
2	Shale Derived No. 2	3.01	61.4	64.4	0.0052	0.106	0.111	1.27
4	Shale Derived No. 2	4.56	75.6	80.2	0.0076	0.126	0.134	1.50

[a]TCO - Total Chromatographable Organics. Materials having boiling points in the range of 100°C to 300°C. See Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht," IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Research Triangle Institute, Research Triangle Park, N.C., EPA-600/7-78-201, October 1978.

[b]GRAV - Gravimetric Analysis.

[c][(TCO)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[d][(GRAV)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[e][(TCO+GRAV)/((Time, min)(DA+FG, m^3/min @ 293.15 K, 101.3250 kPa, wet basis))].

[f]Material extracted from dilution tunnel filter per standard cubic meter of dry flue gas. Volume corrected to 293.15 K, 101.3250 kPa, dry basis.

TABLE 5-10. MODIFIED METHOD 5 SAMPLE TRAIN ORGANIC COMPONENTS -- DIESEL

Run No.	Fuel	XAD-2 Extract		RAC Train Filter GRAV mg	Probe Rinse GRAV mg	Organic Module Condensate		Total (TCO+GRAV) mg	Organic Concentration[c] mg/m³
		TCO[a] mg	GRAV[b] mg			TCO mg	GRAV mg		
1	No. 2, In-House	67.6	6.10	1.25	d	0.420	0	75.37	41.6
5	No. 2, In-House	19.0	2.70	1.12	d	0.286	0	23.11	13.1
3	No. 2, In Barrels	60.3	2.40	0.82	d	0.567	0	64.09	36.4
2	Shale Derived No. 2	33.4	3.20	1.24	d	0.449	0	38.29	21.5
4	Shale Derived No. 2	19.5	3.20	1.20	d	0.736	0	24.64	13.8

[a]TCO - Total chromatographable organics. Materials having boiling points in the range of 100°C to 300°C. See Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht," IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Research Triangle Institute, Research Triangle Park, N.C., EPA-600/7-78-201, October 1978.

[b]GRAV - Gravimetric Analysis. See Reference in footnote "a."

[c][(TCO+GRAV)/(st. vol. in m^3, 293.15 K, 101.3240 kPa, dry basis)].

[d]Combined with RAC Train Filter GRAV.

TABLE 5-11. CORRECTED[a] TCO AND GRAV VALUES -- DIESEL

Run No.	Fuel	Modified Method 5 Sample Train[b]					Dilution Tunnel					Flue Gas Organic Concentration mg/m^3
		Percent Identified	XAD-2 Extract				Percent Identified					
			TCO		GRAV			TCO		GRAV		
			mg	mg/m^3	mg	mg/m^3		mg	mg/m^3	mg	mg/m^3	
1	No. 2, In-House	79	67.6	37.4	5.2	2.9	9.2	2.94	0.0546	64.8	1.2	1.3
5	No. 2, In-House	42	19.0	10.8	2.5	1.4	4.3	2.69	0.0518	106	2.0	2.1
3	No. 2, In Barrels	80	59.0	33.6	1.5	0.91	10	7.00	0.131	118	2.2	2.3
2	Shale Derived No. 2	65	33.4	18.8	3.2	1.8	20	2.72	0.0535	58.0	1.1	1.2
4	Shale Derived No. 2	46	19.4	10.9	3.0	1.7	21	3.47	0.0649	69.1	1.3	1.4

[a]Corrections made for contaminants (silicone, phthalate, and solvent) in identified portions of the extracts.

[b]Includes extracts from XAD-2, probe rinse, RAC train filter, and organic module condensate.

[c]Concentrations uncertain. Sample was spilled during preparation.

The XAD-2 results on the diesel engine show that a relatively consistent high percentage of the organics were identifiable, whereas the data from the package boiler XAD-2 results show the identifiable percentage is more variable. Whether this variability is attributable to fuel type, the boiler combustion process, inconsistent sample concentrations (as previously noted for the package boiler), sample size, contaminant affecting sample size or analysis error could not be determined.

The classes of organics in the package boiler samples are given in Tables 5-12 and 5-13 for the modified Method 5 and dilution tunnels, respectively. Similarly, the class of organics for the diesel engine tests are given in Tables 5-14 and 5-15. The two columns under each fuel type in Tables 5-12 through 5-15 represent replicate runs and provide an indication of repeatability.

From these data it can be seen that the repeatability is not good from the replicate runs for either the package boiler tests or the diesel engine tests. The diesel results do tend to have a more consistent pattern than does the package boiler. This concern was discussed at length during the Phase I workshop (Appendix A).

The results of the PAH spot tests are given in Table 5-16 for the package boiler and Table 5-17 for the diesel engine. With few exceptions these results were negative for the package boiler samples. The diesel engine particulate filter, however, indicated a positive result with almost identical concentrations for all test runs.

5.2.1 Bioassay Analysis

Originally, it was planned to do the Ames tests on each of the dilution tunnel filters, however, due to lack of sufficient quantity of sample and problems in extracting the organics from the particulate material, no bioassay tests were performed during this phase of the program.

TABLE 5-12. ORGANIC CLASS COMPARISON--PACKAGE BOILER, REPLICATED RUNS
XAD-2 Extract, Modified Method 5 Sample Train

Organic Class	Concentration, mg/m^3									
	No. 2, In-House		No. 6, 1.4% S		No. 6, 2.1% S		EDS Middle Distillate		SRC-II Heavy Distillate	
	Run 1R	Run 16	Run 9	Run 14	Run 7R	Run 12	Run 5	Run 11R	Run 13	Run 15
Aliphatic Hydrocarbons										
Alkanes	0.0079	-	-	-	-	-	-	-	-	-
Alkenes	0.06	-	-	-	0.011	-	-	-	-	-
Nitrogen Containing	0.12	-	-	0.22	0.043	0.012	-	0.053	-	-
Aldehydes	-	-	-	-	-	-	0.17	0.024	-	-
Halogenated Aliphatics										
Saturated	0.0079	-	-	-	-	-	-	-	-	-
Ethers										
Unsubstituted	-	0.022	-	-	-	-	-	-	-	-
Alcohols										
R-OH	0.074	0.077	0.2	-	0.074	-	-	-	-	0.14
Esters	-	-	-	-	0.11	-	-	-	-	-
Phthalate	-	0.019	-	-	0.31	-	0.85	-	-	0.49
Ketones	0.039	-	0.034	-	-	-	-	-	-	0.048
Amines										
Aliphatic	0.0072	-	-	-	0.042	-	-	-	-	-
Heterocyclic Nitrogen										
Indoles	0.068	-	-	-	-	-	1.9	-	-	-
Organic Acids	-	-	-	-	0.028	-	-	-	1.3	-
Silicones	0.69	0.058	0.81	0.069	0.098	0.049	5.1	0.11	-	0.063
Total Identified Organic	1.1	0.18	1	0.29	0.78	0.061	8.1	0.19	1.3	0.73
Total Extractable Organic	1.7	0.31	2.6	1.4*	0.88	0.18	8.4	0.38	2.4	0.7
Percent Identified	65	58	38	21	89	34	96	50	54	106

*Concentration uncertain.

TABLE 5-13. ORGANIC CLASS COMPARISON--PACKAGE BOILER, REPLICATED RUNS
Dilution Tunnel Filter

Organic Class	Concentration, mg/m^3									
	No. 2, In-House		No. 6, 1.4% S		No. 6, 2.1% S		EDS Middle Distillate		SRC-II Heavy Distillate	
	Run 1R	Run 16	Run 9	Run 14	Run 7R	Run 12	Run 5	Run 11R	Run 13	Run 15
Aliphatic Hydrocarbons										
Alkanes	-	0.0044	0.0012	-	0.0086	Lost	0.001	0.015	-	0.0017
Alkenes	-	-	-	-	-	-	-	-	-	-
Nitrogen Containing	-	-	-	0.0026	-	-	-	-	-	-
Aldehydes	-	-	-	-	-	-	-	-	-	-
Halogenated Aliphatics										
Saturated	-	-	-	-	-	-	0.00055	-	-	-
Ethers										
Unsusbstituted	-	-	-	-	-	-	-	0.003	-	-
Alcohols										
R-OH	-	-	0.00054	-	0.0015	-	0.00088	0.011	-	-
Esters	-	0.0023	-	-	-	-	-	0.00055	-	-
Phthalate	0.013	0.0013	0.0032	0.0039	0.017	-	0.014	0.019	-	0.015
Ketones	-	-	0.0018	-	0.00088	-	-	0.003	-	0.0016
Amines										
Aliphatic	-	-	-	-	-	-	-	-	-	-
Heterocyclic Nitrogen	-	-	-	-	-	-	0.002	-	-	0.0025
Indoles	-	-	-	-	-	-	-	-	-	-
Organic Acids	-	0.001	-	-	-	-	-	-	-	-
Silicones	-	-	0.012	0.024	0.011	-	0.014	-	0.017	0.0089
Total Identified Organic	0.013	0.009	0.019	0.03	0.04	-	0.032	0.052	0.017	0.03
Total Extractable Organic	0.056	0.0039	0.033	0.0099	0.12	≥ 0	0.2	0.08	0.013	0.062
Percent Identified	23	231	58	303	33		16	65	131	48

TABLE 5-14. ORGANIC CLASS COMPARISON -- DIESEL
XAD-2 Extract, Modified Method 5 Sample Train

Organic Class	Concentration, mg/m^3				
	No. 2 In-House Run 1	No. 2 In-House Run 5	No. 2 In Barrels Run 3	Shale Derived No. 2 Run 2	Shale Derived No. 2 Run 4
Aliphatic Hydrocarbons					
Alkanes	0.77	0.66	1.5	1	2
Nitrogen Containing	0.23	-	0.35	0.15	0.22
PAH Hydrocarbons					
MW < 216	0.46	0.89	0.98	-	0.59
Ethers					
Unsubstituted	10.8	-	1.5	5.4	-
Epoxides	-	-	0.36	-	-
Aldehydes	0.54	0.29	1.8	0.48	-
Alcohols					
R-OH	15.6	0.45	2.9	7	0.83
Esters	-	0.95	8.3	-	0.76
Phthalate	-	-	0.4	-	-
Ketones	2.5	2.1	10.8	0.23	2
Alkyl Sulfur					
Mercaptans	0.53	-	-	-	-
Organic Acids	1.2	-	-	-	-
Silicones	0.5	0.13	0.82	-	0.14
Total Identified Organic	33.1	5.4	29.6	14.3	6.5
Total Extractable Organic	40.8	12.3	35.7	20.6	12.7
Percent Identified	81	44	83	69	51

TABLE 5-15. ORGANIC CLASS COMPARISON -- DIESEL
Dilution Tunnel Filter

Organic Class	Concentration, mg/m^3				
	No. 2 In-House Run 1	No. 2 In-House Run 5	No. 2 In Barrels Run 3	Shale Derived No. 2 Run 2	Shale Derived No. 2 Run 4
Aliphatic Hydrocarbons					
Alkanes	0.018	-	-	0.032	-
Alcohols					
R-OH	-	0.012	0.013	-	0.16
Esters	-	0.012	0.013	-	-
Phthalate	0.06	0.054	0.14	0.16	0.16
Alkyl Sulfur					
Sulfides	0.0032	-	-	-	-
Silicones	0.039	0.026	0.092	0.066	0.13
Total Identified Organic	0.12	0.092	0.24	0.26	0.31
Total Extractable Organic	1.3	2.1	2.4	1.3	1.5
Percent Identified	9.2	4.4	10	20	21

TABLE 5-16. PAH SPOT TEST -- PACKAGE BOILER

Run No.	Fuel	Modified Method 5 Sample Train		Dilution Tunnel Filter	
		XAD-2 Extract	Organic Module Condensate	PAH Test	PAH Concentration mg/m^3
1R	No. 2, In-House	negative	negative	negative	-
16	No. 2, In-House	negative	negative	positive	0.00016 - 0.0016
3	No. 2, In Barrels	negative	negative	negative	-
9	No. 6, 1.4% S	negative	negative	negative	-
14	No. 6, 1.4% S	negative	negative	negative	-
7R	No. 6, 2.1% S	negative	negative	negative	-
12	No. 6, 2.1% S	negative	negative	negative	-
8	No. 6, 2.9% S	negative	negative	negative	-
10	No. 6, 0.7% N	negative	negative	positive	-
10R	No. 6, 0.7% N	-	negative	positive	0.000028 - 0.00028
4R	Methanol	negative	negative	negative	-
6	Shale Derived No. 2	negative	negative	-	-
5	EDS Middle Distillate	negative	negative	negative	-
11R	EDS Middle Distillate	negative	negative	positive	0.0023 - 0.023
13	SRC-II, Heavy Distillate	negative	negative	negative	-
15	SRC-II, Heavy Distillate	negative	negative	negative	-

TABLE 5-17. PAH SPOT TEST -- DIESEL

Run No.	Fuel	Modified Method 5 Sample Train		Dilution Tunnel Filter	
		XAD-2 Extract	Organic Module Condensate	PAH Test	PAH Concentration mg/m^3
1	No. 2, In-House	negative	negative	positive	0.0019 - 0.019
5	No. 2, In-House	negative	negative	positive	0.019 - 0.19
3	No. 2, In Barrels	negative	negative	positive	0.019 - 0.19
2	Shale Derived No. 2	negative	negative	positive	0.02 - 0.2
4	Shale Derived No. 2	negative	negative	positive	0.019 - 0.19

5.3 STATISTICAL ANALYSIS

The data generated from the package boiler was initially found to be difficult to interpret. In order to attempt to identify some degree of confidence in the data a statistical analysis of both the package boiler and the diesel engine tests results was performed by Dr. James E. Dunn, Department of Mathematics and Statistics, University of Arkansas.

The results of the statistical analysis were presented as part of the data summary and operating procedures prepared for the workshop. The main conclusion of the analysis are discussed in the proceedings of the workshop given in Appendix A.

5.4 QUALITY ASSURANCE

A preliminary quality assurance plan as described in the EPA Quality Assurance Measurement Manual was prepared and approved for Phase I of this project. In addition, a safety protocol was also prepared and approved in accordance with the EPA laboratory requirements. There were no deviation from these approved plans during the test program.

SECTION 6.0

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APPENDIX A

PHASE I SYNFUEL COMBUSTION WORKSHOP

PHASE I SYNFUEL COMBUSTION WORKSHOP

March 1983

by

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A-2

ABSTRACT

Phase I testing has been completed in a program designed to develop a protocol for determining environmentally significant differences between petrofuels and synfuels and their combustion emissions. A 589-kW package boiler, and a 186.4-kW stationary diesel were chosen as combustors. Six petrofuels (No. 2 and No. 6 fuel oils) and four synfuels (methanol, shale derived No. 2, Exxon Donor Solvent (EDS) middle distillate, and SRC-II heavy distillate) were chosen for combustion. Continuous monitors measured emissions of O_2, NO, NO_x, CO, CO_2, and THC. Exhaust samples were taken in a modified Method 5 sample train and in a dilution tunnel. Fuel samples and organic extracts from the sample train and dilution tunnel were analyzed for total mass of organic material, PAHs, and organic compounds and classes. Results showed some differences between emissions of petrofuels and synfuels, but also indicated that improved operating procedures needed to be developed to reduce the replication variability. Potentially much of that variability can be reduced by use of a new fuel handling facility and improved combustor operation.

A workshop was held with government agencies and with industrial personnel who have been involved with synfuels manufacturing and/or combustion emission testing of synfuels. Recent test information and experience were exchanged at the workshop. A number of conclusions were drawn about the Phase I testing procedures and results, and recommendations were made to permit development of better procedures in Phase II for determining differences between synfuels and their combustion emissions.

A-3

INTRODUCTION

The purpose of the project was to develop a test procedure to compare the combustion emissions from representative combustors burning prototype synfuels, and petrofuels that the synfuels may replace. Phase I of the project culminated in a workshop, held at EPA/IERL-RTP on August 25 and 26, 1982, in which the procedures used and the data obtained were exchanged for recent test information and experience of selected government-agency and industry personnel engaged in development and/or combustion testing of synfuels. The workshop participants drew certain conclusions from the Phase I testing and made recommendations which may permit the development of more meaningful testing procedures and data assessments in the next phase of the project.

WORKSHOP

The workshop began by reviewing the IERL-RTP Phase I operating procedures. Workshop participants from the Pittsburgh Energy Technology Center, Bartlesville Energy Technology Center, and Exxon reviewed recent studies and experience in their respective institutions relative to testing of synfuels and their combustion emissions. The IERL-RTP data and proposed workshop discussion issues were distributed to the participants several weeks before the workshop itself. The discussion of the workshop issues, the conclusions, and the recommendations for the Phase II study are given in subsequent sections.

The combustors chosen for the IERL-RTP study were a small industrial package boiler (maximum of 2.6×10^9 J/hr steam) and a stationary diesel with a 205 kW generator output. Both combustors were operated at about 80 percent load and at an optimum excess air to minimize smoke or

particulate concentration in the emissions. The fuels selected for the package boiler tests and the stationary diesel tests are listed in Tables A-1 and A-2, respectively.

During the combustor runs and cleaning operations, specified disposable protective clothing and cartridge respirators were used by the operating personnel. Those involved in sample handling, preparation, and analysis were required to follow standard laboratory precautionary procedures.

Fuel samples were taken several months prior to the combustion test and were submitted to ultimate and proximate analyses, heating value determination, and inorganic analysis by spark source mass spectrometry, a semiquantitative PAH spot test, and a total quantitative organic analysis. Fuels were also screened by GC/MS for compound class identification. Combustion emissions were continuously monitored for O_2, CO_2, CO, NO, NO_x, THC, and SO_2. Emission samples were taken in a modified EPA Method 5 sample train and a dilution tunnel. The dilution tunnel took part of the flue (exhaust) gas stream and diluted it with laboratory air in about a 10 to 1 ratio. The diluted (and cooled) flue gas was then filtered through a 0.51- x 0.51-m Teflon-coated fiberglass filter on which particulate and condensed organic material were collected. The modified Method 5 sample train drew a flue gas sample several meters downstream of the dilution tunnel sample point.

The combustion test run cycle began with cleaning of the combustor and flue duct surfaces, where possible, by brushing and vacuuming. No. 2, In-House fuel oil was then burned for approximately 1 hour to bring the combustor to steady state operation. The test fuel was burned for about 2 hours while samples were being taken in the dilution tunnel and the modified Method 5 sample train. The cycle was repeated for the next fuel. For the package boiler runs, a smoke-spot-versus-percent-excess-air curve was determined for each fuel. The percent excess air used for testing that fuel was determined by visually selecting the "knee" in the curve (the point at which the slope of the curve increases rapidly), and adding 1 percent oxygen to that value. The results of organic concentration and particulate concentration for

A-1

TABLE A-1. FUELS BURNED -- PACKAGE BOILER

Petroleum-Based Fuel Oil
No. 2, In-House
No. 2, In Barrels
No. 6, 1.4% S
No. 6, 2.1% S
No. 6, 2.9% S
No. 6, 0.7% N
Synfuels
Methanol
Shale Derived No. 2
Exxon Donor Solvent (EDS) Middle Distillate
Solvent Refined Coal (SRC)-II Heavy Distillate

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TABLE A-2. FUELS BURNED -- DIESEL

Petroleum-Based Fuel Oil
No. 2, In-House
No. 2, In Barrels
Synfuels
Shale Derived No. 2

the dilution tunnel and the modified Method 5 sample train are given in Tables A-3 and A-4, respectively, for the package boiler tests and for the diesel tests. The tables also show which runs were replicated. The chronological order of the runs corresponds with the run number.

The particulate samples collected in the dilution tunnel filter included condensed organic material. The dilution tunnel organic concentration reported for Tables A-3 and A-4 included the TCO and GRAV portions extracted from the filter by methylene chloride. For the modified Method 5 sample train the particulate included solid particles (and associated condensed organic material) collected in the sample probe, the cyclone separator, and on a glass fiber filter in the sample train. Organic material in the vapor phase was collected in a cooled glass module containing XAD-2 resin, the filter, and the organic module condensate.

The organic material from all the samples was analyzed for total organic material above the 100°C boiling range, semiquantitative PAH spot test, and qualitative GC/MS screen. The purpose of using these chemical procedures was to determine if differences between the petrofuel and the synfuel emission samples could be detected using cost effective methods.

The Ames test was the bioassay selected for the test program because it required only a small amount of sample, and it is a relatively simple test. EPA/HERL and others have much experience with this test, expecially with combustion products. No bioassay results were possible, either because there was not enough organic material collected or because of problems encountered in removing particulate material from the filters. It is anticipated that these problems will be resolved by the time Phase II testing begins.

Two major problems became apparent in interpreting the Phase I test results. For both the package boiler runs and the stationary diesel runs, there was a great deal of variability in the results. This was due in part to silicone contamination of the samples, especially for the package boiler. The large amount of variability reduced the sensitivity of comparing differences between fuels. The large silicone contamination of the samples also reduced the ability to measure and to detect fuel-to-fuel differences.

TABLE A-3. SUMMARY EMISSION RESULTS -- PACKAGE BOILER

Run No.	Fuel	Modified Method 5 Sample Train		Dilution Tunnel	
		Flue Gas Organic Concentration mg/m^3	Flue Gas Particulate Concentration mg/m^3	Flue Gas Organic Concentration mg/m^3	Flue Gas Particulate Concentration mg/m^3
1R	No. 2, In-House	2.61	2.81	0.0561	1.25
16	No. 2, In-House	0.321	1.42	0.00389	1.06
3	No. 2, In Barrels	2.49	3.68	0.235	1.64
9	No. 6, 1.4% S	3.78	62.9	0.0332	58.9
14	No. 6, 1.4% S	2.67	120	0.00198	46.0
7R	No. 6, 2.1% S	18.6	367	0.123	135.3
12	No. 6, 2.1% S	1.72	276	≥ 0	219.3
8	No. 6, 2.9% S	29.9	257	$\overline{0.0895}$	130
10R	No. 6, 0.7% N	≥ 1.05	32.4	0.00909	9.73
4R	Methanol	$\overline{4.63}$	2.18	0.0922	0.538
6	Shale Derived No. 2	0.99	43.7	≥ 0.312	2.98
5	EDS Middle Distillate	43.2	146	$\overline{0.196}$	1.32
11R	EDS Middle Distillate	1.08	67.1	0.0798	5.47
13	SRC-II Heavy Distillate	2.84	206	0.0130	7.31
15	SRC-II Heavy Distillate	0.750	6.40	0.0623	6.57

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TABLE A-4. SUMMARY EMISSION RESULTS -- DIESEL

Run No.	Fuel	Modified Method 5 Sample Train		Dilution Tunnel	
		Flue Gas Organic Concentration mg/m^3	Flue Gas Particulate Concentration mg/m^3	Flue Gas Organic Concentration mg/m^3	Flue Gas Particulate Concentration mg/m^3
1	No. 2, In-House	41.6	18.5	1.30	17.1
5	No. 2, In-House	13.1	27.1	2.11	28.2
3	No. 2, In Barrels	36.4	27.5	2.45	27.8
2	Shale Derived No. 2	21.5	21.5	1.27	19.0
4	Shale Derived No. 2	13.8	33.5	1.50	19.6

For each variable measured, it was possible to set 95 percent confidence intervals for a single, new observation or for the mean of two new replications for the following petroleum fuel groups: all petrofuels, No. 2 petrofuels, and No. 6 petrofuels. Any new, untested fuel which falls outside the limits determined in the Phase I study would then warrant further investigation, with the false positive error rate controlled at $\leq$ 5 percent.

Dan F. Ryan of Exxon described three sets of tests with firetube boilers burning EDS fuel oil blends. Two of the tests were with a 490-kW boiler; the third, with a 13,700-kW boiler. The first test had the objective of determining the combustion performance of the boiler with EDS blended fuel oil compared with the petrofuel performance. The results indicated there were no problems regarding flame light off, nozzle fouling, or shutdown. The smoke emissions with EDS were equal to or lower than petroleum reference fuels at all levels of excess air. Particulate emissions were lower than with petroleum reference fuels. PNA emissions were considerably higher with EDS fuel than with petroleum fuel. Combustion tests were performed to identify combustion parameters affecting PNA emissions. Combustor design, nozzle design, atomizing air pressure, and additives were all found to affect PNA emissions. Combustion tests in a large scale (13,700-kW firetube boiler) were designed to compare PNA emissions of EDS fuels with those of a reference petroleum fuel. The PNA emissions were found to be comparable and considerably less than found in the 490-kW boilers. Some tests by Mitsubishi (burning EDS fuel in large boilers and small boilers), confirmed the results of the Exxon tests--PNA emission concentrations from the large boiler were considerably less than from the small boilers.

James M. Eckmann and Curt M. White of the Pittsburgh Energy Technology Center (PETC) described some tests in a 196-kW firetube boiler burning liquid fuels ranging in combustion characteristics from No. 2 to No. 6 petroleum fuel. The synfuel burned was SRC-II. Middle distillate, heavy distillate, and three blends of middle and heavy distillate SRC-II were burned, and the emissions compared to those from the combustion of

A-10

No. 2 and No. 6 petroleum-based fuels. Significant differences in the composition of the trace organics in the exhaust gases were observed as a function of the fuel burned, but total PAH levels were comparable for all fuels. It was found that, even during good combustion conditions, some liquid fuel survived the combustion process and appeared in the duct.

Don Seizinger, of the Bartlesville Energy Technology Center (BETC), described testing that was done on small diesel engines that were to be used in mine applications. The tests involved taking the entire exhaust (about 0.142 m^3/s) through a catalyst bed, a trap, and a water scrubber before venting. The catalyst did not reduce the particulate; the particle size distribution in and out of the catalyst bed was virtually unchanged. The trap used reduced the amount of particulate in the exhaust; the catalyst reduced the PNA level significantly. The exhaust system was also set up to take the exhaust through a dilution tunnel instead of through the trap and water scrubber. The dilution tunnel had a 1.016- x 1.016-m filter to collect particulate and condensed organic in the exhaust. The organic material was extracted with methylene chloride and an ethanol/toluene azeotrope. The extracted material was sent through an atmospheric liquid chromatographic separation and a high-pressure liquid chromatographic separation. The separated fractions were then subjected to the Ames test to identify the mutagenic fractions. Further chemical analyses were conducted on the fractions that were positive on the Ames test.

WORKSHOP ISSUES

The purposes of the workshop were primarily (1) to exchange information on the recent testing of synfuels combustion and their emission products, which has been discussed above, and (2) to discuss issues of interest to the EPA and others in order to permit the development of more meaningful testing procedures and data assessments in the next phase of the project.

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One of the issues discussed was how to select the temperature at which oils should be introducted into the boiler, especially the heavier synfuels. Investigators from PETC used viscosity as a setting. Their experience indicated that each burner was designed for a fuel having a specified kinematic viscosity. For a new fuel, a batch sample was taken a day or so before the test burn. Viscosity as a function of temperature was run for that fuel. The temperature at which the fuel was injected was selected to give the visocity for which the burner was designed. If a temperature greater than 121^{o}C was required, indirect steam heat was used, since electrical heaters tend to coke and clog. It was felt that fuel viscosity was one of the most important independent variables to control for comparing fuels of different composition. The statistical analysis also showed that the atomizing air pressure was another independent variable to control for comparing fuels, and for replicating runs of the same fuel.

Safety protocols were discussed, primarily with respect to protection of personnel operating the combustors and taking and handling samples. It was apparent that the operating procedures for handling hazardous fuels and synfuels were about the same in each laboratory, and that the protocols in use were appropriate. Skin contact with petrofuels, especially the No. 6 fuels, and all synfuels was to be avoided. Disposable plastic-covered-paper protective clothing was generally used. For hazardous spills, the use of gloves, goggles, shoe coverings, and respirators was recommended. Some questions arose as to whether the respirators used were sufficient to remove the organic vapors and particulates encountered with the use of each fuel. The recommendation was made to investigate the matter further. Chuck Sigmund of the Exxon Product Development Department at Linden, NJ, was suggested as a possible source of information relative to the selection of the respirator used when testing EDS fuels.

At PETC, all contaminated fuels (i.e., fuels having suspected carcinogens) are stored in a holding tank equipped with a carbon filter to the outside. A contractor hauls the contaminated fuel to a waste disposal site. At EPA/IERL-RTP the contaminated fuel is burned in the package boiler.

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Some discussion centered on the importance of carryover of material from one test fuel run to the next. No clear conclusion was reached as to whether the cleaning procedure at IERL-RTP between runs, followed by conditioning the boiler surfaces by burning No. 2 fuel for an hour, was sufficient to prevent carryover of contaminants in the emissions from one run to the next.

One suggestion was made, based on some of the testing done at PETC. A fuel was spiked with diisopropylnaphthalene (DIPN) (manufactured by American Cyanamide Company) and burned. Tests indicated that up to 5 percent of the DIPN in the first fuel was required to detect DIPN in the emissions of the next test fuel, when the normal cleaning procedures were followed. The use of DIPN was suggested as a tracer to test whether carryover is a problem in the IERL-RTP experiments. It was understood that the usual cleaning procedures would be used between runs. In studying the problem of carryover from one run to the next, the following questions need to be considered:

1. What is acceptable in terms of carryover?
2. What is the difference in carryover whether or not the cleaning and/or boiler conditioning steps are followed between runs?

Some discussion related to boiler operation at optimum conditions. Boiler data indicated that the operating conditions selected for Phase I testing provided good combustion efficiency over a wide range of fuels. The near optimum boiler operating conditions provided greater than 100-mg samples of particulate material for most of the fuels. The particles contained insufficient amounts of total extractable organic material, however, to perform the Ames bioassay analysis. The rabbit alveolar macrophage (RAM) test was suggested as an optional bioassay. The RAM cytotoxic bioassay procedure can utilize unextracted particles directly, requires no chemical preparation, uses about 500 mg particulate sample per test, and provides another measure of biological response.

It was suggested that because probably only a few commercially operated package boilers would be operating at optimum conditions, it would be important to investigate emissions from off-optimum conditions

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of operation in addition to optimum conditions. Although the boiler may be operated at off-optimum conditions, it could still be operated in an acceptable manner from a regulatory standpoint. The near-optimum conditions can probably be selected to provide the organic extractables required for the Ames mutagenicity tests.

In order to increase the amount of particulate collected (and a corresponding increase in extractable organics), consideration should be given to sample a greater fraction of the stack gases by using larger filters, or using more filters in parallel.

It was noted that determining the Phase I "knee-of-the-smoke-curve" method of selecting the appropriate oxygen level for operation was somewhat arbitrary. On the other hand, it is the technique used by service personnel to set boiler excess air levels. For several fuels, or for a fuel with some uncertainty as to the best selection of the optimum value for oxygen, it was recommended to operate the package boiler at several settings of excess air. Such a series of runs may better indicate the "optimum" condition, and how better to define (or select) it. Exxon chose excess air in their EDS combustion studies by gauging against a low PNA level and adding 2 percent additional oxygen.

An issue addressed by the workshop was whether IERL-RTP should study the combustion of fuel blends. When synfuels are first introduced to the market, blends of synfuels and petrofuels will probably be marketed first; e.g., gasohol. It was generally recognized that presently available synfuels may not be representative of what may be marketed, with the possible exception of some of the EDS fuels.

Fuel blending in drum quantities was discussed. A drum can be put on a roller and rolled for several hours, a stirring blade or paddle can be used, or the fuel can be pumped around a loop. It was recognized that some synfuels cannot be mixed successfully with certain petrofuels, because of phase separation. No general conclusion was reached, nor was IERL-RTP's study of the combustion characteristics of fuel blends recommended.

Regarding when to sample the fuels, the preferred method was to sample the fuel several weeks ahead of the combustion test to determine the main combustion parameters, C, H, S, N, heating value, viscosity,

etc. The recommendation was then to sample the fuel again either the same day as the test, or a day or two before the test for more definitive analysis, such as the chemical class analysis.

IERL-RTP's selection of an appropriate compromise--between method simplicity and the ability to distinguish between petroleum and synthetic fuels and their emissions in their chemical analysis procedures--was discussed. The conclusion was that IERL-RTP's results were not sufficiently discriminatory to determine a difference. PETC advocated a more positive identification of individual chemical components in the fuels and in the emission samples, since there was frequently a correlation between the two. Some workshop participants felt that a compound by compound analysis would not be cost effective unless the differences between the synfuel and petrofuel analogues or their emissions proved to give biological assay results that were different, and it was desirable to identify the compounds causing the differences. Additional chemical procedures that can identify specific nitro-organic and polycyclic organic compounds were suggested for consideration in analyzing future combustion samples.

It was suggested that chemical compound classification systems such as PONA or SARA be considered as alternatives to the one presently used by IERL-RTP. The system used by IERL-RTP suggested that low concentrations of aldehydes, alcohols, and ketones were found in EDS middle distillate; such compounds have never before been reported to be found in EDS liquids.

The question of the potentially hazardous nature of high molecular weight material was recognized as being nebulous. The exact boundaries of the high molecular weight material are not well defined. The extremely high molecular weight materials were not expected to be mutagenic. It was pointed out that perylene, with a 5-ring structure, was known to be mutagenic.

Little opinion was expressed on the importance of TCO and GRAV measurements in characterizing differences. In the statistical analysis it was possible to set 95 percent confidence intervals on the acceptable TCO and GRAV numbers for petrofuels and synfuels. The general conclusion reached was that this particular approach was useful for defining differences and that the method should be developed further.

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Both Exxon and PETC measured PAH (or PNAs) using GC/UV. PAHs were measured as a class since they were usually found in every combustion emission regardless of source. PAHs also contain a very high proportion of mutagenic compounds.

Don Seizinger of BETC outlined some of his experience with various solvents, used in extracting organic materials from diesel particulates:

- Cyclohexane--not very good results. Did not extract much from the particulate.
- Toluene--a good solvent.
- Methylene chloride--good solvent. BETC continued using it since EPA advocated its use.
- Ethanol/benzene azeotrope--Both GM and BETC found this mixture to be particularly useful with shale oil diesel particulates. It seemed to do a better job than $MeCl_2$ in extracting polar material. Its use declined after it was determined that benzene was a very highly toxic material and carcinogenic for humans.
- Ethanol/toluene azeotrope--found to be almost as good as ethanol/benzene azeotrope, yet not so toxic.

The solvent would not be expected to make much difference in extracting organic material from particulate with No. 2 fuel oil. With shale oil particulate, or perhaps some of the other synfuels, methylene chloride might not extract as much as some other solvent.

Regarding the appropriate length of time to extract organic material, the opinion was expressed that a light loading of organic material takes a longer extraction time than a heavier loading. BAP was said to take at least four times the normal length of time to extract. It was said that up to 48 hours was needed to extract some material. It was recognized that it was not possible to get all the absorbed organic material off the particulate or the XAD-2 resin. The opinion was expressed that alkanes were not as strongly absorbed on particulate as on XAD-2 resin.

Ultrasonic vibrations enabled the extraction to be accelerated, but there were problems in that the sonic energy could destroy the filter

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and then make it infeasible to contact with fresh solvent the material to be extracted, as with the normal extraction apparatus.

In discussing the appropriateness of selecting the Ames test as the bioassay planned for the Phase I testing, the fundamental question raised was what was to be measured or tested. With the IERL-RTP's program, the measurement of concern was the mutagenicity differences between petrofuels and synfuels and their corresponding combustion emissions. This fact along with the fact that small sample sizes were expected led to the conclusion that the Ames test was the appropriate bioassay. NitroPAHs are expected to be present in the emissions regardless of which fuel (petrofuel or synfuel) is used. These materials are likely to affect the Ames tests.

Regarding operating the boiler at optimum conditions and what effect this might have on the biological assay results, experience has shown that more toxic and mutagenic material would be expected if the combustion were less efficient.

The emission sample collection procedures were designed to collect organic material condensing at temperatures greater than 100^{o}C. It was likely that some toxic material (e.g., benzene) was thus not collected, or subsequently detected in the chemical (or biological) analysis. The more volatile emissions have not been dealt with in a definitive way and need to be studied in detail at least once. Some BETC studies have carbon numbers on volatile combustion emissions.

The opinion was voiced that the combustor design and performance made more difference in producing mutagenic material in the emissions than fuel differences. BETC cited some studies showing that, for a particular engine, fuel aromaticity was varied from 0 to 40 percent with little change detected in the emissions. A key factor in detecting a difference between fuels is the definition of "difference." More studies need to be made to determine the range of fuels and the range of emissions expected from petrofuels. This would help identify differences between synfuels and petrofuels.

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Collecting large samples and samples with unbiased particulate was discussed. The discussion included the fact that particulate concentration results for the package boiler indicated a higher concentration for the modified Method 5 sample train than for the dilution tunnel by a factor of 2 or higher. This seemed contrary to expectations. Although there was a different arrangment of sample ports between the package boiler runs and the diesel runs, the apparent anomolies were not explained satisfactorily.

The statistical analysis focused on the variability of several variables (e.g. TCO, GRAV, particulate concentration) between replicate runs and between petrofuels and synfuels. Several tests were made to test the hypothesis that the variance of several dependent variables was the same for petrofuels and synfuels. The results showed that it was not possible to make that statement in several cases. Linear and square-root scales were tested to determine if changing scale would make a difference in the test of the hypothesis that the variance between petrofuels and synfuels was the same. Since the square-root scale marginally improved the results, it was used in subsequent analyses.

In most cases the fuel-to-fuel variability was about the same as the replication variability. It was therefore not possible to determine significant fuel-to-fuel differences on that basis.

EPA/IERL-RTP's petrofuel/synfuel handling and conditioning facility was described. The facility will make combustion runs easier with fuels that need heating. Better temperature control will be possible and it will also be possible to lengthen the run by delivering fuel from more than one barrel during the run. It was felt that much of the replication variability of the runs in Phase I, resulted from the inability of the heating equipment to control the temperature before and during a run. The new synfuel/petrofuel handling and conditioning facility is expected to reduce the replication variability greatly, making it easier to detect fuel-to-fuel variability.

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For XAD-2 and dilution tunnel extracts of TCO, GRAV, (TCO+GRAV), TCG, and particulate concentration, it was possible to set up 95 percent confidence limits for any single new observation or the mean of two replications for the package boiler. These limits were set up on three bases: for all petrofuels used in the Phase I study, for the No. 2 fuels, and for the No. 6 fuels. If an unknown fuel were burned, and any of the dependent variables listed above fell outside the 95 percent confidence limits (either for a single measurement or for the mean of two replications) then the probability is 5 percent that the deviation is due to random error, e.g. some different composition or behavior of the unknown fuel is indicated. Thus further testing would be required to determine why there was a difference and what the environmental implications might be.

The statistical analysis then focused on two areas: (1) correlations between dependent and independent variables, and (2) identifying the causes of replication variability. Many relationships were investigated to determine correlations between dependent and independent variables, after adjusting out the mean differences among fuels. For example the square root of the dilution tunnel TCG correlated well (correlation coefficient $R = -0.911$) with the fuel rate, suggesting that variability in fuel rate settings was a major contributor to replication variability in TCG. Linear regression models were also explored with one, two, and three independent variables.

The discussion and results of the statistical studies led to the recommendation that there be further collaboration between the engineers and scientists involved with the project and Dr. James E. Dunn to assist in developing a more meaningful model of the combustion process.

The workshop participants appreciated the contribution the statistical analysis has made in this study. They affirmed that the statistical analysis should be continued to aid in the development of a more meaningful Phase II of the project.

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CONCLUSIONS

- Boiler data indicated that the operating conditions selected for Phase I testing provided good combustion efficiency over a wide range of fuels.
- A need for better control of key independent operating variables was indicated.
- The fuel pumped to the package boiler should be heated to the temperature required to supply the fuel to the burner at the viscosity for which the burner was designed.
- The chemical analyses of the Phase I study were not sufficiently discriminatory to determine a difference between the emissions from petrofuels and their synfuel counterpart.

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RECOMMENDATIONS

- Consider the use of a cytotoxic bioassay such as the rabbit alveolar macrophage (RAM) test as an additional measure of biological response.
- Consider running the package boiler at off-optimum operating conditions which would simulate field operating conditions of similar sized boilers that are poorly maintained and operated.
- Analyze future combustion samples using procedures that can identify specific nitro-organic or polycyclic organic compounds which are known to have greater mutagenic potency.
- Consider sampling a greater fraction of the stack gases by using larger filters, by using more filters in parallel, or by designing a new sampling system that can collect exhaust samples at a faster rate.
- Consider installation of a CO monitor/alarm in the combustion laboratory.
- Consider the use of a fuel spiked with DIPN to determine if carryover from one run to the next is significant, while following the usual Phase I cleaning procedure between runs.
- Investigate the use of a PNA-versus-excess-oxygen graph as an alternate method of setting optimum boiler operating conditions.
- Take a fuel sample for analysis either the same day as the test, or a day or two ahead.
- Consider the use of chemical compound classification system such as PONA or SARA as alternatives to IERL-RTP's present system.
- Consider the use of the measurement of PAH (or PNA) quantitatively as a basis for detecting differences in emissions.

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- Perform additional studies to determine the range of emissions from a wider range of petrofuels.
- Investigate the possibility of some collaborative tests with EPRI in their upcoming large scale tests with EDS fuels.
- Eliminate siloxanes and phthalates from the samples where possible.
- Provide additional engineering guidance to the statistician to assist in deriving more powerful modeling tools; i.e. for identifying independent, dependent, and interdependent variables.
- Reduce the replication variability by better control of key independent operating variables, e.g. fuel injection temperature, air atomization pressure, and excess air.

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LIST OF WORKSHOP ATTENDEES

Dan R. Ryan	Exxon Research and Engineering Company Baytown, TX
Donald Seizinger	U.S. Department of Energy, Bartlesville Energy Technology Center, Bartlesville, OK
Curt M. White	U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA
James M. Eckmann	U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA
James E. Dunn	Department of Mathematics and Statistics, University of Arkansas, Fayetteville, AR
T. K. Rao	Northrop Services Incorporated, Research Triangle Park, NC
James B. Homolya	Energy and Environmental Division, TRW Incorporated, Research Triangle Park, NC
Robert A. McAllister	Energy and Environmental Division, TRW Incorporated, Research Triangle Park, NC

Attendees from the U.S. Environmental Protection Agency, Research Triangle Park, NC:

Industrial Environmental Research Laboratory

Frank T. Princiotta	Joseph A. McSorley	Janet Hopkins
Robert P. Hangebrauck	Ray G. Merrill	Raymond A. Grote
W. Gene Tucker	Michael C. Osborne	Nelson L. Butts
T. Kelly Janes	John H. Wasser, Jr.	Joshua S. Bowen
Robert E. Hall		

Health Effects Research Laboratory

Joellen Lewtas
Ann Austin

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CONVERSION FACTORS

To Convert From	To	Multiply By
Horsepower (boiler)	watt (W)	9.809 500 E+03
Horsepower (550ft-lb_f/s)	watt (W)	7.456 999 E+02
Btu (thermochemical)/hr	watt (W)	2.928 751 E-01
Btu (thermochemical)	joule (J)	1.054 350 E+03
inch (in)	metre (m)	2.540 000 E-02
cfm (ft^3/min)	cubic meter/ per second (m^3/s)	4.719 474 E-04

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PETROFUELS/SYNFUELS WORKSHOP
U.S. ENVIRONMENTAL PROTECTION AGENCY
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA

AGENDA

August 25, 1982

8:30 a.m.	Opening	IERL/RTP
8:40 a.m.	Objectives	Tucker
9:00 a.m.	EPA Synfuel Combustion Testing: Phase 1	
	Project Coordination	McSorley
	Combustion Procedure	Osborne
	Chemistry Procedure	Merrill
	Bioassay Procedure	Lewtas
10:00 a.m.	Break	
10:15 a.m.	Testing by Others: EXXON	
10:45 a.m.	GULF	
11:15 a.m.	PETC	
11:45 a.m.	BETC	
12:15 p.m.	Lunch	
1:15 p.m.	Discussion of Issues (examples attached), Plenary Session	
	Fuel Handling Issues; Discussion Leader	Osborne
1:45 p.m.	Combustion Operation Issues; Discussion Leader	Osborne
2:15 p.m.	Fuel and Emission Sampling Issues; Discussion Leader	Osborne
2:45 p.m.	Break	
3:00 p.m.	Fuel and Emission Analyses Issues, Chemical; Discussion Leader	Merrill
3:45 p.m.	Fuel and Emission Analyses Issues, Bioassay; Discussion Leader	Lewtas
4:30 p.m.	Data Analysis Procedures; Discussion Leader	Dunn
5:00 p.m.	Adjournment	

(continued)

AGENDA (Concluded)

August 26, 1982

8:30 a.m.	Discussion Summaries	McAllister
9:30 a.m.	Group Assignments and Objectives	McSorley
9:40 a.m.	Group A - Fuel Handling and Combustion Testing	
	Leader	Osborne
	Observer	McAllister
	Group B - Sampling and Chemical Analysis	
	Leader	Merrill
	Observer	Homolya
12:00 noon	Lunch	
1:00 p.m.	Data Interpretation	Dunn
1:30 p.m.	Group Recommendations and Summaries	
	Group A	McAllister
1:45 p.m.	Group B	Homolya
2:00 p.m.	General Discussion	McSorley
2:45 p.m.	Concluding Remarks	Tucker
3:00 p.m.	Adjournment	

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PETROFUELS/SYNFUELS WORKSHOP ISSUES

1.0 Fuel Handling

1.1 Are there any aspects of the way the fuels were handled prior to combustion that may have biased the emission test results? How do you decide what temperature to heat a fuel to before burning it? Keep in mind you do not want fuel temperature to bias your results going from fuel to fuel.

1.2 In what ways could the handling of fuels have been improved, especially in connection with safety of operating personnel? What should the protective clothing and respirator requirements be during the handling of synfuel and/or synfuel barrels?

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PETROFUELS/SYNFUELS WORKSHOP ISSUES

2.0 Combustion Operation

2.1 Is there a practical, better way to prevent contamination of the boiler between runs than to clean the boiler tubes after each test and reburn with No. 2 In-House oil for one hour before burning the next test fuel? Does the preheating or conditioning step with No. 2 fuel oil make sense? Is between-run cleaning of the boiler necessary?

2.2 Which package boiler operating parameter or parameters should be varied or held constant in order not to bias run-to-run and fuel-to-fuel results? Consider smoke spot, fuel feed rate, excess air, atomizing air pressure, etc. Was the smoke spot "knee-in-the-curve" approach a reasonable way to obtain a baseline operational setting for the boiler? How do you achieve fuel-to-fuel unbiased off-baseline operation?

2.3 Is it practical for IERL to blend fuels for the diesel engine in order to achieve high enough cetane numbers? Do suppliers use special blending procedures and/or agents which would make their blends different from what we could achieve?

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PETROFUELS/SYNFUELS WORKSHOP ISSUES

3.0 Fuel Emission Sampling

3.1 Were fuel samples obtained properly? Should fuel samples be taken for analysis on the day of the burn from the barrels to be used, or can they be taken ahead of time?

3.2 Is the EPA Method 5 train with an XAD-2 adsorption trap the best practical sampling tool for this application? Consider the small sampling rate of 0.75 cfm, the general availability to the public of other sampling systems, and the types of analyses that can and cannot be performed on the sample. Given the constraints of incomplete particle collection in the dilution tunnel, low flow rate on the EPA Method 5 train, and limited synfuel availability, is it better to get larger samples for biological testing by: 1) sampling several hours longer with the Method 5 train and using all available fuel, 2) operating at potentially biased off spec conditions, 3) continuing to use the dilution tunnel to obtain all bio-test samples, or 4) using another approach.

3.3 For the package boiler runs, the ratio of particulate for the Modified Method 5 Sample Train to the particulate for the dilution tunnel, except for Run 15, is greater than 1.0. Any ideas why this is so? See Table A-5 enclosed. For the diesel runs the ratio appears to be about 1.0, on the average. If the ratio for the package boiler is greater than one, while the ratio for the diesel is indeed one, is this a surprising result? Any postulates why? Why should (or should not) the ratios be the same for package boiler and for diesel runs? If the dilution tunnel filter is not collecting a large fraction of the particulates collected by the EPA Method 5 train, how can the tunnel be modified to collect more "particulate?"

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TABLE A-5. PARTICULATE CONCENTRATION RATIO

Run No.	Particulate Concentration, Dilution Tunnel mg/m^3	Particulate Concentration, Modified Method 5 Sample Train mg/m^3	R[a]
Package Boiler			
1R	1.25	2.81	2.25
16	1.06	1.42	1.34
3	1.64	3.68	2.24
9	58.9	62.9	1.07
14	46.0	120	2.61
7R	135.3	367	2.71
12	219.3	276	1.26
8	130	257	1.98
10R	9.73	32.4	3.33
4R	0.538	2.18	4.05
6	2.98	43.7	14.7
5	1.32	146	111
11R	5.47	67.1	12.3
13	7.31	206	28.2
15	6.57	6.40	0.974
Diesel			
1	17.1	18.5	1.08
5	28.2	27.1	0.961
3	27.8	27.5	0.989
2	19.0	21.7	1.14
4	19.6	33.5	1.71

[a] R = (Particulate Concentration, Modified Method 5 Sample Train)/ (Particulate Concentration, Dilution Tunnel).

PETROFUELS/SYNFUELS WORKSHOP ISSUES

4.0 Fuel and Emission Analyses, Chemical

4.1 Were appropriate physical and compositional properties of the fuels measured?

4.2 Has an appropriate compromise been chosen between method simplicity and the ability to distinguish between petroleum and synthetic fuel emission samples.

4.3 Were appropriate stack gas measurements made?

Were appropriate emission constitutents looked for? How could the organic analytical procedures have been improved? The inorganic procedures? Is there a need to account for a higher percentage of the high molecular weight nonvolatile organics? Does the high concentration of silicone contaminents preclude comparison of synthetic and petroleum fuel emission samples? Should volatile organic materials be included in the screening approach?

4.4 Is the use of FID quantitation and GC/MS qualitiative ID appropriate?

Is the method of relative retention index necessary for the identification peaks of and comparison of GC and GC/MS data?

4.5 What information is critical for the synfuel/petrofuel comparison, e.g., TCO, GRAV, GC/MS compound class ID? What is the best format for comparison purposes? Is the statistical approach used appropriate and useful?

In Table A-6 for diesel runs, except for phthalates and silicones, there seems to be little correspondence between organic classes in the replicated runs for the dilution tunnel filter. For the XAD-2 Extract however, there is considerably better correspondence in the replicated runs for organic classes, as shown in Table A-7 for the diesel runs. Any clues as to why? The assumption is that there should be better correspondence in the dilution tunnel data. Is that a valid assumption? In Tables A-8 and A-9 there seems to be little correspondence in organic classes for replicated runs. Is this an expected or surprising result? Should there be a better correspondence?

4.6 Is there a reason for reevaluation of the use of organic solvents used in the extraction of residual organics from various types of particles? Are residual organics on diesel particles (or boiler particles) of a nature such that they might be better extracted with something other than methylene chloride? Does the acidity, basicity, polarity, or neutrality of the solvent under consideration influence the potential for artifact production during the extraction procedure?

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TABLE A-6. ORGANIC CLASS COMPARISON -- DIESEL
Dilution Tunnel Filter

Organic Class	Concentration, mg/m^3				
	No. 2 In-House Run 1	No. 2 In-House Run 5	No. 2 In Barrels Run 3	Shale Derived No. 2 Run 2	Shale Derived No. 2 Run 4
Aliphatic Hydrocarbons					
Alkanes	0.018	-	-	0.032	-
Alcohols					
R-OH	-	0.012	0.013	-	0.16
Esters	-	0.012	0.013	-	-
Phthalate	0.06	0.054	0.14	0.16	0.16
Alkyl Sulfur					
Sulfides	0.0032	-	-	-	-
Silicones	0.039	0.026	0.092	0.066	0.13
Total Identified Organic	0.12	0.092	0.24	0.26	0.31
Total Extractable Organic	1.3	2.1	2.4	1.3	1.5
Percent Identified	9.2	4.4	10	20	21

TABLE A-7. ORGANIC CLASS COMPARISON -- DIESEL
XAD-2 Extract, Modified Method 5 Sample Train

Organic Class	Concentration, mg/m^3				
	No. 2 In-House Run 1	No. 2 In-House Run 5	No. 2 In Barrels Run 3	Shale Derived No. 2 Run 2	Shale Derived No. 2 Run 4
Aliphatic Hydrocarbons					
Alkanes	0.77	0.66	1.5	1	2
Nitrogen Containing	0.23	-	0.35	0.15	0.22
PAH Hydrocarbons					
MW < 216	0.46	0.89	0.98	-	0.59
Ethers					
Unsubstituted	10.8	-	1.5	5.4	-
Epoxides	-	-	0.36	-	-
Aldehydes	0.54	0.29	1.8	0.48	-
Alcohols					
R-OH	15.6	0.45	2.9	7	0.83
Esters	-	0.95	8.3	-	0.76
Phthalate	-	-	0.4	-	-
Ketones	2.5	2.1	10.8	0.23	2
Alkyl Sulfur					
Mercaptans	0.53	-	-	-	-
Organic Acids	1.2	-	-	-	-
Silicones	0.5	0.13	0.82	-	0.14
Total Identified Organic	33.1	5.4	29.6	14.3	6.5
Total Extractable Organic	40.8	12.3	35.7	20.6	12.7
Percent Identified	81	44	83	69	51

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TABLE A-8. ORGANIC CLASS COMPARISON--PACKAGE BOILER, REPLICATED RUNS
XAD-2 Extract, Modified Method 5 Sample Train

Organic Class	Concentration, mg/m^3									
	No. 2, In-House		No. 6, 1.4% S		No. 6, 2.1% S		EDS Middle Distillate		SRC-II Heavy Distillate	
	Run 1R	Run 16	Run 9	Run 14	Run 7R	Run 12	Run 5	Run 11R	Run 13	Run 15
Aliphatic Hydrocarbons										
Alkanes	0.0079	-	-	-	-	-	-	-	-	-
Alkenes	0.06	-	-	-	0.011	-	-	-	-	-
Nitrogen Containing	0.12	-	-	0.22	0.043	0.012	-	0.053	-	-
Aldehydes	-	-	-	-	-	-	0.17	0.024	-	-
Halogenated Aliphatics										
Saturated	0.0079	-	-	-	-	-	-	-	-	-
Ethers										
Unsubstituted	-	0.022	-	-	-	-	-	-	-	-
Alcohols										
R-OH	0.074	0.077	0.2	-	0.074	-	-	-	-	0.14
Esters	-	-	-	-	0.11	-	-	-	-	-
Phthalate	-	0.019	-	-	0.31	-	0.85	-	-	0.49
Ketones	0.039	-	0.034	-	-	-	-	-	-	0.048
Amines										
Aliphatic	0.0072	-	-	-	0.042	-	-	-	-	-
Heterocyclic Nitrogen										
Indoles	0.068	-	-	-	-	-	1.9	-	-	-
Organic Acids	-	-	-	-	0.028	-	-	-	1.3	-
Silcones	0.69	0.058	0.81	0.069	0.098	0.049	5.1	0.11	-	0.063
Total Identified Organic	1.1	0.18	1	0.29	0.78	0.061	8.1	0.19	1.3	0.73
Total Extractable Organic	1.7	0.31	2.6	1.4*	0.88	0.18	8.4	0.38	2.4	0.7
Percent Identified	65	58	38	21	89	34	96	50	54	106

*Concentration uncertain.

TABLE A-9. ORGANIC CLASS COMPARISON--PACKAGE BOILER, REPLICATED RUNS
Dilution Tunnel Filter

Organic Class	Concentration, mg/m^3									
	No. 2, In-House		No. 6, 1.4% S		No. 6, 2.1% S		EDS Middle Distillate		SRC-II Heavy Distillate	
	Run 1R	Run 16	Run 9	Run 14	Run 7R	Run 12	Run 5	Run 11R	Run 13	Run 15
Aliphatic Hydrocarbons										
Alkanes	-	0.0044	0.0012	-	0.0086	Lost	0.001	0.015	-	0.0017
Alkenes	-	-	-	-	-	-	-	-	-	-
Nitrogen Containing	-	-	-	0.0026	-	-	-	-	-	-
Aldehydes	-	-	-	-	-	-	-	-	-	-
Halogenated Aliphatics										
Saturated	-	-	-	-	-	-	0.00055	-	-	-
Ethers										
Unsusbstituted	-	-	-	-	-	-	-	0.003	-	-
Alcohols										
R-OH	-	-	0.00054	-	0.0015	-	0.00088	0.011	-	-
Esters	-	0.0023	-	-	-	-	-	0.00055	-	-
Phthalate	0.013	0.0013	0.0032	0.0039	0.017	-	0.014	0.019	-	0.015
Ketones	-	-	0.0018	-	0.00088	-	-	0.003	-	0.0016
Amines										
Aliphatic	-	-	-	-	-	-	-	-	-	-
Heterocyclic Nitrogen	-	-	-	-	-	-	0.002	-	-	0.0025
Indoles	-	-	-	-	-	-	-	-	-	-
Organic Acids	-	0.001	-	-	-	-	-	-	-	-
Silicones	-	-	0.012	0.024	0.011	-	0.014	-	0.017	0.0089
Total Identified Organic	0.013	0.009	0.019	0.03	0.04	-	0.032	0.052	0.017	0.03
Total Extractable Organic	0.056	0.0039	0.033	0.0099	0.12	≥ 0	0.2	0.08	0.013	0.062
Percent Identified	23	231	58	303	33		16	65	131	48

PETROFUELS/SYNFUELS WORKSHOP ISSUES

5.0 Fuels and Emissions Analyses, Bioassay

5.1 Was the appropriate bioassay used?

5.2 What artifacts that are likely to appear in the samples would influence the Ames tests?

5.3 The package boiler and the diesel were operated at optimum efficiency conditions. Would these conditions be expected to result in high mutagenicity in the emission products?

5.4 How can we overcome the bioassay sample preparation problems associated with solvent exchanging and resultant toxicity of samples containing methylene chloride?

5.5 How could we evaluate the mutagenicity of the gaseous organics not collected on XAD? Is that important?

5.6 Is there any evidence that fuel composition influences the chemical characterization of the emissions or the mutagenicity?

5.7 As long as the variation in combustion runs is so high, would bioassay data be meaningful?

5.8 How should the mutagenicity be expressed (e.g., per mg particle emission or per kg fuel emission)?

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PETROFUELS/SYNFUELS WORKSHOP ISSUES

6.0 Data Analysis Procedures

6.1 What steps need to be taken to reduce the replication variability?

6.2 Fuels

Do the data jibe with expected values? What are the physical and compositional differences between synfuels and petrofuels that are most likely to affect combustion emissions?

6.3 Combustor Conditions

Do the data sufficiently describe how the combustors were being operated? Was combustor operation appropriately stable for experimental baseline purposes? Table A-10 shows a summary of the silicone content of the XAD-2 Extract and the Dilution Tunnel Extract in chronological order. The silastic gasket on the package boiler door was removed between Runs 9 and 10R. Although there appears to be a smaller amount of silicone concentrations in the XAD-2 Extract values after Run 10R, the same does not appear to be the case for the dilution tunnel runs. Is this as would be expected? Why or why not? Examining silicone values for the XAD-2 Extract for the diesel runs (in Table A-10), it is clear they are higher than the dilution tunnel values. Is this an expected result? Why or why not?

6.4 Emissions

What seem to be the major qualitative or quantitative differences in emissions (from run to run, from fuel to fuel, or from combustor to combustor)? What are the most likely causes of these differences? What anomolies in the data are there? Are there any areas where greater attention to quality assurance would have been especially helpful? Is there evidence (e.g., in the chemical data) of run-to-run contamination? What method(s) of formatting the emissions data would have made its review easier?

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A-10

TABLE A-10. SILICONE CONTENT

Run No.	XAD-2 Extract mg/m^3	Dilution Tunnel mg/m^3
Package Boiler		
1R	0.69	-
3	0.31	-
4R	0.38	0.0045
5	5.1	0.014
6	0.25	-
7R	0.098	0.011
8	25.9	0.0064
9	0.81	0.012
10R[a]	-	0.0016
11R	0.11	-
12	0.049	-
13	-	0.017
14	0.069	0.024
15	0.063	0.0089
16	0.058	-
Diesel		
1	0.50	0.039
2	-	0.066
3	0.82	0.092
4	0.14	0.13
5	0.13	0.026

[a]Run 10R was the first run made after silastic was cleaned from the package boiler door.

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APPENDIX B

PHASE I MEASUREMENT EQUIPMENT AND PROCEDURES

Auxiliary Supplies and Equipment

Monitors for O_2, CO, and CO_2 were Beckman instruments; the NO/NO_x monitor operated on a chemiluminescence principle; the SO_2 monitor was a pulsed fluorescence instrument.

Flue gas was dried by running flue gas through a Hankinson cooler followed by a $CaSO_4$ cartridge for CO, CO_2, and O_2 monitors. All other monitors sampled wet flue gas.

Smoke spots were formed by drawing flue gas at a rate of 9050 mL/minute for 48 seconds (a total of 7240 mL) through a white filter paper for the standard Bacharach smoke spot test. The smoke spot numbers were measured with a R.A.C. reflectometer.

The dilution ratio in the dilution tunnel was calculated from laminar flow meters mounted in the dilution air intake, and in the exhaust from the dilution tunnel. The latter instrument measured the flow rate of dilution air plus flue gas (DA + FG) leaving the dilution tunnel. The other flow meter measured the flow rate of the dilution air (DA) into the dilution tunnel. Both readings were corrected to 70°F (294.26 K) and 1.0 atmosphere pressure (101.3250 kPa), wet basis. The dilution ratio (DA + FG)/FG was calculated as follows:

$$(DA + FG)/FG = (DA + FG)/[(DA + FG) - (DA)].$$

Dilution Tunnel filters (Teflon-coated fiberglass mats of about 20" x 20") were dried in a 150°F oven, allowed to cool in a desiccator, and weighed on an analytical balance. The first 15 filters weighed averaged 10.9387 g with a standard deviation of ±0.04201 g. One filter placed in aluminum foil and weighed seven times gave an average weight of 29.71 g with a standard deviation of ±0.00373 g.

Modified Method 5 Sample Train filters were made of glass fiber. They were prepared for use by firing at 1000°F and allowed to cool in a desiccator prior to weighing. The filters were weighed with and without foil.

Filter Handling

1. Dilution filters were folded into one-eighth the original size by three folds, being careful not to shear at the folds. Careful handling was required and the filters were inspected several times during handling for ruptures.

2. Filters were heated in an air convection oven at 150°F for twenty-four hours to remove any residual moisture. Filters were placed in a desiccator.
3. Filters were weighed on a Mettler analytical balance by balancing on the pan taking care that no filter surfaces touched the balance enclosure.
4. Filters were enclosed in aluminum foil and weighed again.
5. Both the filter weight and the filter plus foil weights were recorded. During handling of the filter during the test run, if a piece of the aluminum foil was lost, the sample collected on the filter could still be determined from the known filter weight alone. For most cases the filter-foil combined weights were used because better reproducibility could be achieved than using the filter weight alone, and since losses could occur by filter handling.
6. The filter and foil was placed in a desiccator for storage until ready for use. When preparing for a run enough filters were weighed (and the weights recorded) for the expected loading.
7. Repetitive weighing of filters in the foil indicated a reproducibility of plus or minus three milligrams for the same filter-foil combination.
8. Filters for use in the Modified Method 5 Sample Train were heated to 1000°F in a muffle furnace then cooled in a desiccator.
9. Train filters were weighed alone and in a handling foil and both weights were recorded for the reason stated in (5).
10. Reproducibility of the weights of the train filters with or without the foil was about one milligram by repetitive weighing.

Train Preparation

1. All glassware was cleaned using the Level 1 Procedure (IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201, October 1978); soap wash in sonic bath, deionized water rinse, 50/50 H_2SO_4/HNO_3 rinse; deionized water rinse, methyl alcohol rinse followed by methylene chloride rinse and oven drying.
2. The stainless steel probe was washed by brushing with soap and water followed by deionized water rinse, and methyl alcohol and methylene chloride rinses.

3. The probe was placed on the train impinger module provided and connected to the glass cyclone.
4. A weighed eleven-centimeter filter was placed in an appropriate filter body and clamped to the cyclone in the heating chambers of the R.A.C. train.
5. A condenser module for XAD-2 resin was loaded by pouring the cleaned resin into the chamber beneath the frit. The XAD-2 resin was held in place by a predried glass wool plug.
6. The XAD-2 module was clamped in place and the lower connecting arm was clamped in place to obtain proper attitude of the condenser module. The upper connecting tube was placed between the filter and the condenser and clamped in place.
7. The first Greenberg-Smith impinger was loaded with 100 mL of deionized water by pouring in the side arm of the impinger from a 100-mL graduated cylinder.
8. The second impinger was an unbroken impingement eductor and 100 mL of deionized water was added to it also.
9. The third impinger was left empty to act as a collector to protect the 200 g of silica gel in the fourth impinger from water carry-over.
10. All connecting tubes were clamped in place and the train was transported to the site for leak testing.
11. To begin the leak testing procedure, the Modified Method 5 Sample Train was connected to the vacuum pump module by the quick connect provided.
12. Prior to leak testing the bypass valve was opened to place the pump in minimum vacuum mode.
13. Slowly the bypass valve was closed until the vacuum reached fifteen inches of mercury vacuum, as specified for leak testing. Any reduction in vacuum at this point allowed the water to backup into the XAD module necessitating reassembling the train.
14. If the leak rate was 0.02 ft^3/minute or less the train was ready. If it maintained this leak rate heated, as well, it was ready for a run.

15. The velocity of the exhaust stack was determined by a pitot tube determination at the stack centerline averaged over time. The sampling rate was then determined from the stack temperature, static pressure, velocity and water vapor content by means of a nomograph.
16. Runs were monitored as closely as possible over a two-hour period.
17. Normal pertinent run parameters were recorded for ultimate volume correction, and subsequent reporting.
18. The entire train was then shut down at the end of two hours and transported to the laboratory for disassembly.

Train Disassembly

1. Two pint jars were appropriately labeled XAD-2 and condensate to contain the two portions of the Modified Method 5 sample.
2. The first step at disassembly was the weighing of a glass beaker to contain the probe rinse. This was accomplished by successive washings of the probe with methylene chloride, and collecting the wash liquid in a weighed beaker.
3. The probe was then cleaned by placing in the sink and running a brush rod through it several times, followed by water, methanol and methylene chloride rinses, in preparation for the next run.
4. The cyclone was removed from the oven housing and washed into the probe rinse breaker provided there was no obvious loading in the catch Erlenmeyer.
5. Cyclone catch if removable was weighed on foil prior to washing into the catch beaker.
6. The glass filter body was removed and placed in a simple dissassembly carriage and the filter was removed and placed in a handling foil and placed in a desiccator for weighing the next day.
7. A clean jar marked XAD-2 was utilized to contain the XAD-2 resin removed from the condenser module. The glass wool plug was removed first, washed with methylene chloride and thrown away. The XAD-2 was removed by tapping and washing with methylene chloride until nearly all was removed.
8. The jar was capped with a cap having a teflon liner.

9. A clean 500-mL graduate was placed adjacent to the condensers. The first water impinger was poured into the graduated cylinder by successive decantation until little or no water could be removed.
10. The wash liquid from the second impinger was poured into the same graduate and, the third likewise. The water amount was recorded on sheets provided and the condensate was poured into the labeled condensate jar and capped.
11. The resulting samples were refrigerated or transferred to the analyst.
12. The following day the train filter and the tunnel filter were weighed and recorded and transferred to the analyst.
13. The train was cleaned as before and prepared for a subsequent run.
14. The probe rinse breaker was placed in a desiccator and weighed after proper desiccation in an appropriate desiccator.

Continuous Monitors

1. Chart drives were turned on and appropriate valves were set to purge gases from the previous day's run.
2. Carbon monoxide, carbon dioxide and oxygen were monitored by Beckman instruments. Carbon monoxide and carbon dioxide instruments were non-dispersive infrared analyzers. The oxygen analyzer was a paramagnetic instrument.
3. In order to zero the instruments, purified nitrogen was used. Nitrogen was allowed to flow until an unwavering zero baseline was reached.
4. Once the zero was established a span gas was allowed to flow to set the upper limit. In the case of oxygen, filtered room air was used to span the instrument at 21 percent oxygen or room air equal to 100 percent of full scale. This procedure was continued until the baseline and upper limit could be reproduced usually within 1 or 2 line widths of the chart. Sufficient time was given to allow equilibration of flow to achieve good instrument response.
5. Carbon monoxide was usually calibrated with carbon monoxide in nitrogen to give 100 full scale equal to 1000 ppmv.
6. Carbon dioxide was calibrated with 15 percent CO_2 in nitrogen so that the CO_2 full scale was 20 percent.

7. The hydrocarbon analyzer was calibrated the same way using propane of a known amount in nitrogen to give a full scale reading of 100 equal to 100 ppmv.
8. The chemiluminescent NO/NO_x analyzer was calibrated with a known NO-in-nitrogen mixture so that a full scale reading was 250 ppmv.
9. No calibration was done for the NO_x measurement. Before each run the NO_x catalytic converter switch was turned on. During a run, NO_x readings were made by turning a switch which sent the entire sample stream to the recorder through the NO_x catalytic converter. Any difference in reading before and after the NO_x switch was turned was attributed to NO_2.

SAMPLE HANDLING AND ANALYSIS

Handling of samples received from IERL/CRB for processing in the Synfuel Utilization Program is described briefly below. Reference to published procedures is made whenever possible.

Sample Preparation

1. Samples were received by the sample custodian, were recorded in the Laboratory sample logbook (logged in) and were scheduled for preparation.
2. Sample processing was started immediately, or samples were stored at 4°C in a refrigerator.
3. Filter samples, XAD-2 resin and particulate catch were Soxhlet extracted for 24 hours with dichloromethane as per EPA 600/7-78-201 Level 1 Procedures Manual.

   Sorbent Trap. The XAD-2 resin from the sorbent trap was removed from the train cartridge and homogenized. The resin was extracted with methylene chloride to remove organic material as follows. The resin was transferred to a previously cleaned glass extraction thimble. A glass wool plug was used to secure the resin, which would otherwise float on the methylene chloride. The boiling solvent in the flask was examined periodically because additional methylene chloride was needed to replace that lost by wetting the resin and by volatilization. The resin was extracted for 24 hours. If water was extracted from the XAD-2 resin during

this procedure, as evidenced by two phases in the liquid portion, they were segregated with a separatory funnel before concentrating the methylene chloride. The aqueous fraction from this separation was added to the condensate catch before it was extracted at the two pH levels.

4. Aqueous condensate from the XAD-2 module was extracted at two pHs (pH 2 and pH 10) with dichloromethane.
5. Organic extracts were concentrated to 10 mL using a Kuderna-Danish apparatus equipped with a 3 ball Snyder column. In some cases, extracts were further concentrated to 1 mL by Kuderna-Danish or under a stream of nitrogen.

Sample Analysis

1. Dilution filters condensate extracts and XAD-2 extracts were subjected to TCO analysis using a Perkin Elmer Sigma 115 GC with FID detection as specified in EPA 600/7-78-201.
2. Aliquots from Method 5 filter sample, particulate sample, and probe rinse extracts were evaporated to dryness in pre-weighed aluminum pans to determine "GRAV" organic concentrations as specified in EPA 600/7-78-201.
3. Aliquots of extracts from dilution filters and XAD-2 resin samples were brought to dryness in preweighed aluminum pans to determine "GRAV" as specified in EPA 600/7-78-201.

The following was adopted from EPA 600/7-78-201:

Quantitative analysis of moderately volatile materials (b.p. 100°C to 300°C) was achieved by a gas chromatographic procedure applied to various organic solvent extracts, organic liquids, and sorbent module rinses. Quantitative analysis of nonvolatile organic sample components (b.p. >ca. 300°C) in all extracts was achieved by evaporating an aliquot of extract to dryness and weighing the residue (GRAV procedure).

TCO analyses of extracts and organic liquids were performed prior to concentration. The appropriate stage to conduct each of these steps (gravimetric analysis, concentrate) depended on the quantity and solubility of the sample as described in the following sections.

Total Chromatographable Organics (TCO) Analysis. The TCO analysis was applied to all samples that might contain compounds in the volatility range of compounds boiling between 100°C and 300°C. These included organic liquids (fuels), dilution filter sample extracts, aqueous sample extracts, and extracts from the train sorbent module samples. However, particulate samples collected at the specified 250°F train oven temperature or residues from high temperature processes did not require TCO analysis.

Because materials in the TCO volatility range were lost to varying degrees during solvent evaporation, it was important that this analysis be performed on extracts and solutions prior to any concentration step.

For determination of TCO, a 1- to 5-μL portion of the extract was analyzed by GC using a flame ionization detector. A 1.8 m x 3 mm O.D. (6 ft x 1/8 in.) column of 10 percent OV-101 on 100/120 mesh Supelcoport was used for this analysis. The GC was operated isothermally at 50°C for 5 minutes after sample injection and then programmed at approximately 20°C/minute to 250°C and held at 250°C as long as necessary for complete elution of sample. Injector temperature of 300°C and detector temperature of 300°C were used.

Quantitative calibration of the TCO procedure was accomplished by use of mixtures of known concentrations of the normal hydrocarbons C_{10}, C_{12}, and C_{16}. The quantitative calibration standards were prepared to cover the concentration range. Retention time limits corresponding to the TCO range of boiling points were defined by the peak maxima for n-heptane (C_7, b.p. 98°C) and n-heptadecane (C_{17}, b.p. 303°C). Therefore, integration of detector response began at the retention time of C_7 and terminated at the retention time of C_{17}. By this procedure, the integrated area covered material in the boiling range of 100°C to 300°C. (The C_7 and C_{17} peaks were not included in the quantitative calibration.)

In the TCO analyses, total integrated area for samples was corrected by subtracting the area of solvent blank prepared (i.e., concentrated) in the same manner as the samples.

The results of each TCO analysis was reported as one number, in milligrams, corresponding to the total quantity of material in the 100° to 300°C boiling range in the original sample collected. The TCO data were thus analogous to the results obtained by gravimetric analysis. The chromatograms themselves contained some additional data beyond the TCO values (i.e., retention times and areas of individual peaks) and were retained.

Gravimetric (GRAV) Analysis. The gravimetric analysis was used for quantification of organic sample components with boiling points higher than 300°C. This analysis was done after the sample extract had been concentrated, since it is recommended to weigh at least 10 mg of sample in a gravimetric analysis, when possible. (Weighing to a precision of 0.1 mg was done.) Sample and tare weights were obtained by drying to "constant weight" (±0.1 mg). For extracts concentrated to 10 mL, a 1-mL aliquot was taken for GRAV analysis. The GRAV results were reported as one number for the entire sample.

Concentration of Extracts and Solvent Exchange Procedure. After the initial TCO analysis (on all samples except particulate fractions and residues from high temperature processes), it was necessary to concentrate the organic extracts to a volume of 10 mL for subsequent analysis. Concentration to slightly less than 10 mL volume (i.e., 8 or 9 mL) was accomplished using a Kuderna-Danish apparatus with a 3-ball Snyder column for volumes less than 1 L, and a rotary evaporator for volumes that initially exceeded 1 L. It was essential that the extract not be reduced to dryness at this point in the scheme to prevent loss of TCO range material. The concentrated extract was transferred to a convenient graduated container (e.g., Kuderna-Danish receiver or centrifuge tube) and the volume restored to 10 mL. The concentration process was stopped if material began to drop out of solution. In that case, the extract was restored to a convenient volume in which the material was redissolved. The original TCO analysis (on all samples except particulate fractions and residues from high temperature processes) provided guidance as to the degree

of concentration that was required for each particular sample. The objective was to achieve a final concentration of not more than 100 mg/mL and a final volume of not less than 10 mL.

At this stage in the analysis sequence, a GRAV determination was done and the TCO determination (on all samples except particulate fractions and residues from high temperature processes) was repeated (unless the initial TCO values for the unconcentrated extract exceeded the guideline of 40 mg/L TCO). A 1-mL aliquot was used for the GRAV analysis and a 5-µL aliquot was used for the TCO. If 40 mg/L was not achieved, concentration was continued to 1 mL followed by TCO analysis. Samples were never taken to less than 1 mL total volume.

4. XAD-2 extracts were subject to GC/MS analysis using an HP 5993 GC/MS with electron impact ionization at approximately 70 EV. A packed column of methylsilicone (SP 2100) was used for GC separations. Temperature programming was similar to TCO analyses. Data were collected between 40 and 500 m/e and stored via an HP 21 MX computer on a 7900-24 sector hard disk.

Data Interpretation

1. GRAV results were acquired in duplicate, were averaged, and were corrected for blank.
2. TCO results were based on a calibration curve generated using members of a homologous series of hydrocarbons from C_7 to C_{17}. A linear regression line was calculated using a Sigma 15 data station and calibration was accepted if correlation coefficients were greater than or equal to 0.97. TCO results were corrected for silicone and phthalate contaminants.
3. GC/MS results were interpreted with the aid of computer searching and the Eight Peak Index (primarily the latter). The results reported for peaks above 3 percent full scale represent the best estimate of compound or compound type. No standards or pure compound spectra were used to confirm identification on Phase 1 of the Synfuel Utilization Project.

Sample Disposition

Sample remaining after analysis were transferred to amber screw-cap bottles and stored in the freezer of a conventional refrigerator.

Data Storage

All hard copies of raw data from GC and GC/MS analyses are stored in a central file. GC/MS traced and GC data remain on disk, or tape until after the upcoming workshop.

BIOASSAY PROCEDURES

Bioassay Ames Test

The Salmonella typimurium plate incorporation assay was to be performed as described by Ames (B. N. Ames, J. McCann, and E. Yamasaki, "Methods for Detecting Carcinogens and Mutagens with the Salmonella/Manmmalian Microsome Mutagenicity Test," Mut. Res., 31, 347 (1975) with a minor modification. The modification was to be a minimal addition of the concentration of histidine directly to the plate media instead of to the overlay and that the plates were to be incubated for 72 rather than 48 hours.